



# CHEMICAL ABSTRACTS

Vol. 17.

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## 1—APPARATUS

C. G. DERICK

A new method for the control of thermostats. D. J. AND J. J. BRAVER. *Ind. Eng. Chem.* 15, 359-61(1923).—The sparking at the contact of a mercury-contact regulator bulb is avoided by using a current of only 20 microamperes and amplifying to about 10 milliamperes by a triode tube. This method is preferred to the use of a H atm. around the contact. With this feeble current the contact may be allowed to chatter with impunity; the advantage of a Gouy regulator is thus obtained. The chattering is simply provided by the shaking caused by the stirring. It is necessary to prevent the relay from working too rapidly; hence its action is retarded by the insertion of a condenser.

W. P. WHITE

Errors in the use of thermometers. B. BLOCK. *Chem. App.* 10, 9-11, 19-20 (1923); 12 cuts.—Thermometers for taking temps. inside of vessels or pipes should have long stems and narrow bulbs with thin walls and be inserted well within the walls of the app., and care taken to protect them from spurting of superheated solids. In taking temps. of gases and liquids flowing through pipes they should be inserted at a bend in the pipe so that the flow is against the end of the bulb.

J. H. MOORE

An automatic direct-reading laboratory scale for weighing briquets. H. G. SCHURCHT. *J. Am. Ceram. Soc.* 6, 491-5(1923).—A double-lever scale of 150 g. capacity is described. Av. accuracy is 0.05 g.

C. H. KERR

New form of melting-point apparatus. H. A. BELL. *Ind. Eng. Chem.* 15, 375 (1923).—A modification of the Thiele app.

F. J. C.

Freezing-point determinations on small quantities of liquid with Dekhuyzen's cryoscope. D. G. COHEN-TERRVAERT. *Onderz. physiol. Scheikunde* 1, 35-7(1921); *Physiol. Abstracts* 7, 82.—Dekhuyzen's cryoscope (C. A. 3, 852) presents various advantages over the Beckmann app., and was originally intended for 40 to 50 cc. of liquid. The author obtains good results with a modification, using only 3 cc.

H. G.

New apparatus for washing gases. A. ERNESTA. *Chem. Listy* 16, 274-6(1922).—The tube leading the gas to be purified into the washing vessel is surrounded by a long spiral; this increases the contact of the gas with the liquid and ensures efficient washing. The tube leading in the gas and the spiral are easily removed from the vessel.

J. S. C. I.

Piezo-micrometer and its applications to testing paper, etc. J. STRACHAN. *Proc. Tech. Sect. Papermakers' Assoc.* 3, 20-32(1922).

J. S. C. I.

Evaporator design. Influence of the properties of aluminium sulfate solutions (BADGER, FRANCE) 18.

Acetylene generator. C. WIERDMANN. U. S. 1,447,195, Mar. 6.

Acetylene generator. J. S. NOHL. U. S. 1,447,396, Mar. 6.

Rotary inclined horizontal drying drums. G. B. DAMON. U. S. 1,447,929, Mar. 6. The drum is adapted for drying coal, loam, clay or ores and is heated by combustion gases the temp. of which is equalized before passage to the drier by heat-storage elements, e. g., checkerwork, arranged in series, to maintain a more nearly uniform temp.

**Cleansing condensers and similar apparatus.** F. G. MARTIN. U. S. 1,447,096, Feb. 27. Condensers such as those which may have been used for condensing steam from engines are filled with a 5% or weaker aq. soln. of  $\text{HNO}_3$  and the soln. is circulated through the app. by a pump to remove scale or incrustation. The acid soln. is then withdrawn and the app. is thoroughly rinsed out with circulating  $\text{H}_2\text{O}$ . Cf. *C. A.* 16, 3.

**Apparatus for carbonating water or other liquids.** J. PHILIPPI. U. S. 1,447,884, Mar. 6. The app. comprises a rotating drum contg. foraminous plates over which the liquid to be carbonated is distributed, mounted within a chamber in which ice may be placed and provided with connections through a pair of hollow shafts for supply of  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

**Chemical filters.** C. S. BRADLEY. Can. 228,781, Feb. 20, 1923. A filter has a foundation contg. a conduit and thereon filter bricks having interior chambers for distributing pressure and suction within the bricks and passages providing communication between said chambers and the conduit.

**Filter screens.** A. T. STUART. Can. 228,533, Feb. 6, 1923. A filter screen comprises an open frame with thin sheet material extending across the frame and presenting the edges to the open sides of the frame to support the screens.

**Removable-top continuous kiln.** T. B. MOATS. U. S. 1,447,682, Mar. 6.

**Graphite crucible.** HIROSUKE NAKAMURA, KOZO NAKAMURA and HIKOSHIMA RUTSUO KABUSHIKI KAISHA. Japan 40,310, Oct. 18, 1921. The wall of the crucible forms V-shaped layers; it is manufd. by the machine described in 39,334. Owing to the special construction of the wall, it is resistant to changes of temp. and is very durable.

**Selenium cell or bridge.** C. W. CHERRY. U. S. 1,447,646, Mar. 6. A disk base or backing is employed with a plurality of conductive strips, *e. g.*, of Cu or German silver, wound in a compact coil with interposed insulation on one face and with a layer of Se applied to the surface of the winding. The cell is adapted for measuring intensity of light.

**Apparatus for agitating leather coatings or other liquids.** H. HOUGH. U. S. 1,447,849, Mar. 6. A trough and another receptacle are both provided with power-driven agitators and are connected so that liquid can be circulated from one to the other.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

**Edmund Bouty.** MARCEL BRILLOUIN. *Ann. phys.* 18, 475-83(1923).—Obituary. E. H.

**Georg Lunge.** E. BERL. *Chem.-Ztg.* 47, 157-8(1923).—Obituary. E. H.

**William H. Nichols.** CHAS. R. SMITH. *Ind. Eng. Chem.* 15, 424-5(1923).—A brief biography, with portrait. E. J. C.

**The chemical work of Pasteur.** GABRIEL BERTRAND. *Bull. soc. chim.* 33, 135-54 (1923). E. H.

**The American Institute of Chemistry.** H. G. BYERS. *Chem. Age* (N. Y.) 31, 49-50(1923). E. H.

**Balancing chemical equations.** JAMES H. RANSOM. *Science* 57, 147-8(1923).—A criticism of the algebraic method of balancing equations (cf. *C. A.* 16, 4113). Though it may have a restricted use, it should not be adopted in teaching, for it fails to stress chem. principles and facts, or the mechanism of reactions. C. C. DAVIS

**A relation between the atomic numbers and the atomic weights of the chemical elements.** F. LOEWINSON-LESSING. *Compt. rend.* 176, 307-9(1923).—The difference between the at. wt. of an element and the sum of its at. no. and the at. no. of the immediately following element, is called the *at. difference,  $\delta$* . For the first 20 elements, starting with He,  $\delta$  is 0, or  $\pm 1$ . Starting with Sc,  $\delta$  increases and attains a value of 51 at

U, although in certain groups of elements it remains nearly const. An analogous relation holds for the difference,  $\Delta$ , between the at. wt. of an element and the double of its at. no. These relations permit the prediction of the at. wts. of the 5 unknown elements, the correction of at. wts. which are provisional, the correction of at. wts. of elements whose values of  $\delta$  or  $\Delta$  present a sensible deviation from those of the group which they are associated, and the verifying of isotopes. R. H. LOMBARD

**A revision of the atomic weight of silicon.** The analysis of silicon tetrachloride and tetrabromide. G. P. BAXTER, P. F. WEATHERILL AND E. W. SCRIPTURE, JR. *Proc. Am. Acad. Arts Sci.* 58, 245-68(1923).—The feature of the method for prep. the samples is the careful fractional distn. out of contact with the air and at varying pressures. A progressive change of at. wt. is found from samples at different stages of the process. The final results show great consistency, agreeing to about 1 part in 2000 for a number of detns. and yield a value of 28.063, which is considerably lower than the older accepted value. E. D. WILLIAMSON

**Comparison of the atomic weights of terrestrial and meteoric nickel.** II. Analysis of nickelous chloride. G. P. BAXTER AND F. A. HILTON, JR. *J. Am. Chem. Soc.* 45, 694-700(1923); cf. C. A. 15, 1429.—By the analysis of the chloride, Ni from the Cumpas meteorite is found to possess the same at. wt. as the terrestrial material. E. D. WILLIAMSON

**The specific gravity of anhydrous nickelous chloride.** The determination of specific gravity by displacement of air. G. P. BAXTER AND F. A. HILTON, JR. *J. Am. Chem. Soc.* 45, 700-2(1923).—The sp. gr. as found by displacement of air and of toluene was 3.52 and 3.54, resp. E. D. WILLIAMSON

**Survey of existing crystal structure data.** R. W. G. WYCKOFF. *J. Franklin Inst.* 195, 183-210(1923).—Review concerning the crystal structure of the elements and of inorg. compds. not salts. JOSEPH S. HEPBURN

**Analysis of crystal structure by X-rays.** W. T. ASTBURY. *Science Progress* 17, 386-405(1923).—Review. JOSEPH S. HEPBURN

**The analytical expression of the results of the theory of space groups.** R. W. G. WYCKOFF. *Carnegie Inst. Publ.* 318, 180 pp.(1922).—In giving an analytical expression to all of the special, as well as general cases of the space groups, all of the possible co-ordinate positions which atoms can occupy in any crystal are defined. In an introduction some of the most essential ideas of the theory of space groups are briefly outlined. RALPH W. G. WYCKOFF

**Effect of the form and dimensions of the sample upon the accuracy of X-ray crystal analysis by the powder method.** L. W. MCKEEHAN. *J. Franklin Inst.* 193, 231-42(1922).—"Both theory and expt. indicate that, when great accuracy is desirable in the analysis of highly absorbent crystals, a thin plate is preferable to a circular cylinder. If a cylindrical form is unavoidable, the smallest diam. which gives a measurable photograph will be found to be the best." JOSEPH S. HEPBURN

**The crystal structure of hydrazine dihydrochloride.** R. W. G. WYCKOFF. *Am. J. Sci.* 5, 15-22(1922).—From Laue photographic and spectrographic data and the results of the theory of space groups the manner of arrangement of the atoms within the unit cube of a crystal of  $N_2H_4Cl_2$  has been detd. This unit contains 4 chem. mols. and is 7.89 Å. U. on an edge. The corresponding space group is  $T_h^*$ . The parameter defining the positions of the Cl atoms is 0.27+ and the most probable value of the N parameter is estd. as about 0.04. RALPH W. G. WYCKOFF

**The chemical reactions of crystals and their relation to the molecular structure.** F. RINNE. *Z. Metallkunde* 13, 401-6(1921).—A theoretical paper dealing with the arrangement of the atoms and mols. in crystals and their relation to the symmetry of the crystal. The action of reagents on crystals takes place in a symmetrical manner and



if carried out slowly results in the development of symmetrical figures on the surface of the crystals which vary according to the relation of the face attached to the axes of the crystal. An explanation of this and of the change of crystal form that some minerals undergo on heating is given, based on the space-lattice theory of crystal structure.

J. C. S.

**The valences that stabilize the crystal lattices of elementary substances and of the compounds among metals.** M. PADOA WITH B. ZANELLA. *Gazz. chim. ital.* 52, II, 189—202(1922).—The identity between the chem. valence of C and the bonds between C atoms of crystals of diamond and graphite raises the problem as to the nature of the valence by which the crystals of metals and metalloids are constructed. The idea of attributing this to the principal chem. valences encounters difficulties. P. and Z. review many of the existing data and give some results of their own expts. If the crystal structure is due to the principal valences, the metallic atoms in the solid state will be ions, but all the existing data point away from such a condition. The hypothesis that best conforms with existing data is that in the metallic state the elements have zero valence like the noble gases. The crystal lattice is constituted solely from secondary valences. C thus holds a peculiar place among the elements in this respect. The behavior of metalloids is simply explained if it is admitted that in the metalloid state the principal valences give rise to the formation of the mols. while in the metallic state they have 0 valence like the metals. Isomorphism among metallic elements of the same group is due to the equivalence of the no. and direction of the secondary valences that establish the lattice. In a similar way the secondary valences can explain the formation of compds. between metals. Crystal lattices and stoichiometric relations are discussed in connection with diagrams and spectrographs of alloy crystals with X-rays. The existence of an infinite no. of isomers is provided for in the lattices. With the cubic lattice it is explained how the properties of a metallic alloy may vary extensively with the same compn. In discussing the deviation of compds. with ultramicroscopic granules from the law of definite proportions (cf. Quartaroli, *C. A.* 17, 687) *pyrrhoite* ( $\text{Fe}_4\text{S}_4 - \text{Fe}_{10}\text{S}_{17}$ ) is mentioned, in which the excess S has been attributed to the formation of solid solns. of  $\text{FeS}_2$  in  $\text{FeS}$ . This may be considered as a microcryst. structure with granulation differing according to the samples and with incomplete polygons; thus 2 complete hexagons and one external S atom constitute  $\text{Fe}_4\text{S}_4$ , and 6 complete hexagons and 1 external S atom  $\text{Fe}_{10}\text{S}_{17}$ . P. and Z. have obtained indications on the state of combination of metallic alloys in the solid state, at least for some metallic sulfides and arsenides, by means of the data from electrolytic attacks. When a metallic anode is attacked by an anion (cf. Bolton, *Z. Elektrochem.* 2, 183 (1895)) it frequently happens that the compd. with the lower valence is formed and only in cases of passivity is the form with higher valence obtained. This fact put in relation with the structure of the crystal lattice of the electrode suggests that in the metallic state the atoms ought to be in a state of combination with a valence probably less than, but not greater than that of the attacking ion. In the electrolysis of a Cu electrode in NaI the formation of  $\text{Cu}^+$  is shown, even if  $\text{CuI}_2$  is first formed, by the presence of free  $\text{I}_2$  in the soln. It was thought that these considerations could be extended to other substances used as sol. electrodes. The exptl. results, which cannot be briefly abstracted, appear to confirm the views of P. and Z. on the condition of the valences in these substances.

E. J. WITZEMANN

**Some properties of graphite.** R. M. BURNS AND G. A. HULERT. *J. Am. Chem. Soc.* 45, 572—8(1923).—The ds. of various graphites were detd. by the liquid immersion method. The d. of pure graphite is about 2.20, and that of Acheson graphite about 2.30. The  $\rho$  of C produced by the explosion of graphitic acid indicates that it is probably graphite. Completion of the "drift" or increase in wt. during immersion in the

liquid was hastened by pressure, and the tendency to drift was largely destroyed by compression before the detn. of d.

H. JERMAIN CRICHTON

**The compressibility of thirty metals as a function of pressure and temperature.** P. W. BRIDGMAN. *Proc. Am. Acad. Arts Sci.* 58, 166-242; *Proc. Nat. Acad. Sci.* 8, 361-5(1923).—A new method is described giving higher accuracy than has been obtained hitherto. The change of compressibility and thermal expansion with pressure is proportionally greater than the change of vol. The theoretical views of Born are discussed.

E. D. WILLIAMSON

**Theory of the structure and polymorphism of silica.** R. B. SOSMAN. *J. Franklin Inst.* 194, 741-64(1922).—"It is believed that the  $\text{SiO}_2$  atom-triplet maintains a certain degree of individuality in its amorphous and cryst. states as well as in its compds., and the freedom of its O atoms to change their positions with respect to the silicons is restricted. The triplets are assumed to assemble into chains or threads in the liquid and glassy states, and a thread structure persists in the cryst. states. The 3 principal cryst. modifications (cristobalite, tridymite, quartz) are built up by combining the threaded triplets in 3 different ways, the connection between threads being through the O atoms. The high-low ( $\alpha$ - $\beta$ ) inversions in all the forms are thought to be due to the same underlying mechanism, namely, a change in the state of motion of certain electron orbits, resulting from increased thermal vibration of the atoms, whereby the shape of the  $\text{SiO}_2$  triplet and the relative positions of the two O atoms are suddenly altered."

JOSEPH S. HEPBURN

**Method for the determination of the melting point of metals which fuse at high temperatures.** M. PIRANI AND H. ALTERTHUM. *Z. Elektrochem.* 29, 5-8(1923).—For the detn. of the m. p. a bar of the metal 7 mm. in thickness is used. This has a small boring which is oblique to its axis. The boring is employed as a black body in the temp. measurement. Fusion is indicated by the molten metal running from the boring. Values for the m. p. of tungsten and molybdenum obtained by this method are, resp.,  $3660 \pm 60^\circ$  and  $2840 \pm 40^\circ$ . The sources of error of the method are discussed briefly.

H. JERMAIN CRICHTON

**Rectilinear diameter of neon.** E. MATHIAS, C. A. CROMMELIN AND H. KAMERLING ONNES. *Compt. rend.* 175, 933-5(1922).—A continuation of the work on A, O, N and H (C. A. 16, 4100). The app. was the same as that used previously. The method of purification of the Ne is described. The following typical values were obtained:

T°K.	$\delta$ (obs.) liquid.	$\delta'$ (obs.) Satd. vapor.	$\gamma$ (obs.) = diam. (obs.).	$\gamma$ (calcd.) = diam. (calcd.).
25.17	1.23824	0.00534	0.62179	0.62106
33.09	1.08832	0.03831	0.56331	0.56438
43.02	0.74866	0.23935	0.49401	0.49323

The calcd. values were obtained from the equation:  $\gamma$  (calcd.) =  $-1.154406 - 0.00716146 \Theta$  where  $\Theta = ^\circ \text{C}$ . The angular coeff. of the diam.,  $\alpha = 0.00716146$ , is exceptionally large. The crit. coeff. is  $R\Theta\Delta/\pi = 3.249$ , the smallest value yet found exptly. From the small deviations between calcd. and obs. values it is concluded that Ne obeys the law of rectilinear diam.

E. P. WIGHTMAN

**Atmolysis of a gaseous mixture having several constituents. Application to the mixture used in the manufacture of sulfuric acid by the contact process.** EDOUARD URBAIN AND REMY URBAIN. *Compt. rend.* 176, 304-7(1923).—By applying Graham's law of diffusion the following general equation was developed:

$$\sum_{\lambda=1}^{\lambda=n} \tau_{\lambda} r_{\lambda} \sqrt{\frac{m_{\mu}}{m_{\lambda}}} \omega \sqrt{\frac{m_{\mu}}{m_{\lambda}}} - 1 = 1.$$

$\tau$  is the initial mol. concn.,  $r$  is the enrichment of any gas in a mixt. of  $\lambda$  gases and

is defined by the ratio final/initial mol. concn. of the gas, *e. g.*, the *μ*th gas, *M* is the mol. wt. and  $\omega$  is the ratio of the total final to the total initial mol. concn. after diffusion for a time *t*. When applied to the mixt. of gases used in the contact process, this equation becomes  $\tau_{SO_2} [T_{N_2} (\tau_{SO_2} \omega)^{0.6118} + \tau_{O_2} (\tau_{SO_2} \omega)^{0.4142} + \tau_{SO_3}] = 1$ . The calcd. value for  $\tau_{SO_2}$  was 1.49 and the value found was 1.27. The results varied slightly with the nature of the surface and very decidedly with moisture.

H. M. McLAUGHLIN

**Separation of a liquid mixture by distillation and atmolysis combined. Obtainment of practically pure ethyl alcohol and nitric acid.** EDOUARD URBAIN and REMY URBAIN. *Compt. rend.* 176, 166-8(1923).—The app. consisted of a distg. flask surmounted on a porous porcelain tube surrounded by a jacket fitted so that a vacuum sufficient to cause diffusion of the vapors may be created. A condenser and a 3-way stopcock was attached to this porous tube so that the residual vapors when condensed may be returned to the distg. flask or collected in a receiver. The constituent with the higher mol. wt. will remain in the residual vapors. (Cf. Lord Rayleigh, *Phil. Mag.* 42, 493(1896).) EtOH, 99.8% pure, was obtained from a mixt. of EtOH and H<sub>2</sub>O; and HNO<sub>3</sub>, 99.6% pure, from a mixt. of HNO<sub>3</sub> and H<sub>2</sub>O. The purification was made in 2 steps because the residual vapor condensed from a dil. EtOH mixt. and from a const. boiling HNO<sub>3</sub> mixt. is collected separately but that from a concd. EtOH mixt. and from a dil. HNO<sub>3</sub> mixt. is returned directly to the distg. flask as described above. H. M. McLAUGHLIN

**Theoretical derivation of the vapor-pressure curve of xylene.** D. C. EDWARDS. *Chem. Met. Eng.* 23, 157-8(1923).—Vapor-pressure curves are plotted from all the available data for C<sub>8</sub>H<sub>6</sub>, PhMe and C<sub>10</sub>H<sub>8</sub>. A series of pressures read from the curves is then plotted against the ratio of the corresponding abs. temp. to the abs. b. p. These curves are practically identical. Since the above compds. have curves of the same shape, it is assumed that C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> does also. The vapor-pressure curve of the latter is derived by working backwards from this assumption. E. P. WIGHTMAN

**Vapor pressures of mixtures of water, alcohol and ether at 0°.** J. DESMAROUX. *Mem. poudres* 19, 322-38(1922).—This paper contains the following data for the system water-alcohol-ether, all at 0°: (1) Vapor pressures, (2) densities, (3) compns. of immiscible layers at equil., (4) temps. of sepn. into two layers. E. W. WASHBURN

**Vapor pressure of copper oxide and of copper.** EDWARD MACK, G. G. OSTERHOFF and H. M. KRANER. *J. Am. Chem. Soc.* 45, 617-23(1923).—The rate of oxidation of Na<sub>2</sub>SO<sub>3</sub> by dissolved O to Na<sub>2</sub>SO<sub>4</sub> is affected by extremely small quantities of Cu. This catalysis is used for the *detn. of small quantities of Cu*. The vapor pressure of CuO has been found by the dynamic method to be about 10<sup>-7</sup> mm. at 600°; 10<sup>-4</sup> mm. at 800°; 7 × 10<sup>-4</sup> mm. at 900°; and 10<sup>-4</sup> at 1000°. The calcd. heat of vaporization of CuO in the region 600-800° is 63,000 cal. The v. p. of Cu at 810°, almost 1200° lower than any previously recorded data is at least 5 × 10<sup>-7</sup> mm. JAMES M. BELL

**The colloid concept.** THOMAS BLACKADDER. *J. Am. Leather Chem. Assoc.* 18, 54-60(1923).—An elementary discussion of the colloid state, whose boundaries are assumed to be detd. by the degree of dispersion of the substance. J. A. WILSON

**The province of chemistry in colloidal research.** F. SEKERA. *Chem.-Zig.* 47, 69-71(1923); cf. Traube, *C. A.* 16, 2051; Eibner, *C. A.* 16, 4357.—The mechanism of the formation of colloids was studied in connection with the reaction: AgNO<sub>3</sub> + KI = AgI + KNO<sub>3</sub>. The theories relating to aggregation, coagulation and stability of colloids are reviewed. H. M. McLAUGHLIN

**Colloid chemistry and photochemistry.** KARL SCHAUM. *Kolloid Z.* 31, 258-62(1922).—A survey pointing out the intimate relation between photochemistry and colloid chemistry and how the development of the former has been influenced by the latter. HARRY B. WEISER

**General nephelometry.** M. U. C. AL. LEDNICKY. *Kolloid.-Z.* 32, 12-7(1923).—The conditions under which the concn. of the colloid is inversely proportional to the nephelometer reading are deduced mathematically from Rayleigh's equation for the intensity of the Tyndall effect. The conclusions are verified exptly. with several toxin solns. F. L. BROWNE

**The nature of gels.** S. C. BRADFORD. *Nature* 111, 200-2(1923).—The many theories of gel structure fall naturally under three heads: (1) one-phase or mol. systems, (2) two-phase liquid-liquid systems, and (3) two-phase liquid-solid systems. According to the first, gels are solid solns. which may consist of tenuous interlacing crystals. According to the second, gels are composed of two liquid phases. But emulsions do not have the properties of gels and no liquid-liquid system can be imagined with the elastic properties of gels. The third class assumes that both solid and liquid phases are present. Attempts to calc. a mathematical network have been unsuccessful, probably, because gels with different elastic and thermal properties have different frameworks. von Weimann's work indicates that gelation is merely an extreme case of crystn. Gelatin jelly is a mass of ultramicroscopic spherites of gelatin in which water is held by mol. attraction. Gelatin, even when molecularly dispersed, will be colloidal because of the large size of its mol. Spherites grown to the size of  $3\mu$  were examd. with polarized light. When the nicols were crossed they became brilliantly colored and showed shadow crosses. This indicates that they are really crystal. F. L. BROWNE

**The constitution of colloidal gels.** J. DUCLAUX. *Bull. soc. chim.* 33, 36-43 (1923).—Irreversible gels such as silica gel are composed of a solid sponge of ultramicroscopic dimensions filled with a liquid phase. A reversible gel contains in addn. a third substance, sol. in the liquid phase, whose mols. are too large to pass through the walls of the solid phase, but are small enough to exert a measurable osmotic pressure. Swelling depends upon absorption of solvent through the cell walls, acting as semi-permeable membranes. A gel may be reversible with respect to one solvent and irreversible with respect to another, as for example nitrocellulose in ether or water. In this case the third substance, sol. in ether, is insol. in water. Both nitrocellulose and rubber gels have been sepd. into a sol. and an insol. portion. F. L. BROWNE

**Gelatin.** T. S. PRICE. *Science Progress* 17, 406-15(1923); *Nature* 110, 286-8.—Review of recent work on the physical chemistry of gelatin. JOSEPH S. HEPBURN

**Diffusion in gelatin.** (Contribution on the Liesegang phenomenon.) C. A. SCHLEUSSNER. *Kolloid.-Z.* 31, 347-52(1922).—The form of the rings depends little on the dichromate-ion concn. but largely on the quality and diln. of the gel used. The finer structures in the light rings depend on the formation of halides or phosphates due to impurities in the gel. A. MUTSCHERL

**Some novel aspects of colloidal protection.** JEROME ALEXANDER. *Ind. Eng. Chem.* 15, 283-5(1923).—After a brief review of previous investigations, and a possible explanation of immunity and anaphylaxis, the following new types of colloidal protection are considered: (1) double or plural protection, where protectors are added to more than one of the reacting substances; (2) autoprotection, where a substance in aggregating protects itself; (3) cumulative protection, where numerous substances form a mutually dependent protective chain. The application of these novel principles to many problems in biology, medicine and technology is indicated, e. g., glass, alloys, gluten, proteins, etc. JEROME ALEXANDER

**Studies on protective colloids.** 12. Gelatin as a protective colloid. III. Colloidal platinum. A. GUTHRIE AND A. ZWEIGLE. *Kolloid.-Z.* 31, 346-7(1922).—To 0.14% gelatin sol. (A) (preserved with chloroform) 0.1%  $H_2PtCl_6$  soln. (B) was added and reduction was effected by adding freshly prepd. 0.1% hydrazine hydrate soln. (C).

When equal parts of *A* and *B* were used and the soln. was reduced by adding *C* drop by drop at room temp., a brownish black, translucent sol was obtained. When dialyzed a small irreversible residue formed. The filtrate was stable, could be boiled and evapd., forming a black partially reversible residue. Evapd. *in vacuo* below 40° it was fully reversible but the sol was not as stable as the primary colloid sol. Reduction of 5 parts *A* and 4 parts *B* gave a more stable product but it still gave a slight ppt. during dialysis. The evapd. residue was 70% reversible. It contained 18.76% Pt. 1 part *B* and 5 parts *A* gave a very stable sol. Electrolyte addn. produced sedimentation only after several days. Evapn. in a vacuum gave a reversible product with 55.67% Pt.

A. MUTSCHILLER

**Hydrous oxides. IV. Hydrous stannic oxide.** H. B. WEISER. *J. Phys. Chem.* 26, 654-86(1922); cf. *C. A.* 16, 3418.—The so-called stannic and metastannic acids are hydrous stannic oxides the composition and properties of which are detd. by conditions of formation.  $\text{SnO}_2$  pptd. at ordinary temp. is a loose hydrous mass that is readily peptized by dil. acids and alkalies, forming a colloidal soln., and is dissolved by concd. acids and alkalies forming salts. When formed at higher temps. the oxide is less compact, less sol. and less easily peptized. The oxides formed under different conditions are not mixts. of varying amts. of  $\alpha$ -oxide peptizable by  $\text{HNO}_3$  and  $\beta$ -oxide not peptizable by  $\text{HNO}_3$ , but are chem. individuals which differ from each other in the size of the particles and the structure of the mass and hence in adsorbability, mordanting action, ease of peptization and soly. There are no definite hydrates of  $\text{SnO}_2$ . Mixts. of the hydrous oxides of Fe and Sn in certain proportions are sol. in  $\text{NH}_4\text{OH}$ . This is due to the fact that hydrous  $\text{SnO}_2$  is peptized by  $\text{OH}^-$  and the colloid formed adsorbs hydrous  $\text{Fe}_2\text{O}_3$ , carrying the latter into colloidal soln. Hydrous  $\text{SnO}_2$  peptized by  $\text{HNO}_3$  ages and so coagulates spontaneously. If peptized by a suitable mixt. of  $\text{HNO}_3$  and  $\text{FeCl}_3$  coagulation does not take place on standing or boiling on account of the stabilizing action of the strongly adsorbed  $\text{Fe}^{+++}$  ion.  $\text{SnO}_2$  jellies were prepd. by coagulation of colloidal solns. of the oxide with suitable concns. of electrolyte. HARRY B. WEISER

**The conditions of stability of lyophile colloids.** H. R. KRUYT. *Kolloid-Z.* 31, 338-41(1922).—Both hydration and elec. charge are factors of stability of lyophile colloid particles. Addn. of electrolytes and dehydrating agents (alc.) act independently in the sense of polar grouping of electrolyte mols. on the surface of colloid particles as it is expressed in the Langmuir-Harkins surface-orientation theory. A. M.

**The nature of swelling. VII. Molar relations for swelling and heats of swelling.** E. KNOEVENAGEL. *Kolloidchem. Beihefte* 17, 51-71(1922); cf. *C. A.* 17, 1362.—Swelling equil. studies of systems of acetylcellulose in binary mixts. of diff. concns. showed that the molar concn. of the absorbed liquid or liquid mixts. divided by the moles of acetylcellulose within the system was always a const. Parallel thermal studies of these swelling systems showed that the kg.-cals. liberated per mole acetylcellulose divided by the total moles of absorbed liquid was always a const. This thermal const. was the same for alc., alc.-benzene and nitrobenzene as swelling media, *vis.*, 0.114 cal./mol.

I. NEWTON KUGELMASS

**The velocity of coagulation of selenium sols.** H. R. KRUYT AND A. E. VAN ARKEL. *Kolloid-Z.* 32, 29-36(1923).—The expts. were performed for the purpose of applying v. Smoluchowski's theory of the velocity of coagulation (*C. A.* 11, 3140) to suspensoid sols other than Au, particularly to a sol exhibiting a considerable variation in the velocity of coagulation with concn. of electrolyte. Se sol was made by reducing  $\text{SeO}_2$  with  $\text{N}_2\text{H}_4$ . The dispersity can be controlled by seeding with a "nucleus sol." The sols alter slowly in the dark, becoming more sensitive to electrolytes. In direct sunlight they are coagulated in a few hrs. The exptl. methods were those used by Zsigmondy for Au sol (*C. A.* 12, 2270). The theory of v. Smoluchowski holds in the region

of electrolyte concn. in which the velocity of coagulation does not differ greatly from the velocity for completely discharged particles. For KCl and BaCl<sub>2</sub> this lies in the region of rapid coagulation at the high concns. of 80 and 4 millimoles per l., resp. At lower electrolyte concns. the coagulation takes place more slowly than the theory demands. At the higher concns. of electrolyte the velocity of coagulation is inversely proportional to the concn. of the sol, in agreement with theory. By cataphoresis expts. it is shown that the charge on the particles is still large in the presence of 20 millimoles KCl per l. With BaCl<sub>2</sub> discharge is effected at about 30 millimoles per l. With Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>2</sub> the charge is reduced to 0 at 6.5 millimoles per l. and is reversed at greater concns.

F. L. BROWN

Glue bubbles. CARL BARUS. *Science* 57, 151-3(1923).—Improvements in the U-gage interferometer (cf. *C. A.* 15, 3918) allowed measurements of the surface tension of bubbles formed from glue solns. The tension in spherical bubbles increased rapidly at first, remained const. for a certain interval and then slowly decreased. When const. the bubble was practically solid and the compressed air diffused outward through the colloid. The apparent decrease in tension indicated that the solid bubble was leaky, though continuous. After 4 hrs. no internal pressure remained. With pear-shaped bubbles, the initial increase in tension was more rapid and reached a higher value. On diln. the tension remained low until a very low concn. was reached, whereupon it rapidly increased. No bubbles could be obtained from this very dil. soln. after 1 week, but addn. of NaOH restored this property. Graphs show the quant. results.

C. C. DAVIS

Colloids and ions. WOLFGANG OSTWALD. *Anales soc. espan. fis. quim.* 20, 283-340(1922); *Kolloid-Z.* 32, 1-12(1923).—The dispersity of colloids may result from soly. conditions, as when mastic sol is prepd. by addn. of the alc. soln. to H<sub>2</sub>O; from the velocities of nucleus formation and crystn. as in the prepn. of gold sol; or from the chem. grouping of atoms in complex mols. such as the proteins. In the last case not only the no. of atoms but their arrangement in space is of importance. Where the linking of atoms into colloid aggregates is due to these primary affinities the colloids are generally more stable than those due to secondary affinity groupings. Where the colloid character is thus due to chem. nature the materials are called *eu colloids*. Systems in which the dispersity varies continuously with concn. or temp. are called *disintegration colloids*. Soap, gelatin and many dyestuffs belong to this class. *Electrosomes* are defined as movable, material carriers of electricity. They include electrolytic ions, which follow Faraday's and Ohm's laws and the fundamental law of the dissociation theory, and colloidal electrosomes. The charges on the colloid electrosomes may be due to contact potential, electrolytic dissociation, adsorption, or electro-kinetic potential. Peculiarities of colloid electrosomes are: (a) they may be regarded as ionization products one of whose ions is very large; Faraday's law fails with these; (b) frequently there is transfer of matter in only one direction as the elec. current passes; (c) the charge associated with a given substance may be either positive or negative; (d) the amt. of charge on a single particle may vary enormously and may be as great as 2000 elementary charges; (e) the mobility under unit potential gradient is variable. *Isolabile* colloids depend for their stability on the presence of a charge, *isostable* colloids are stable in the absence of charge. Electrosomes play an important part in the behavior of the former. With highly charged, weakly hydrated, isolabile colloids such as colloidal gold, oppositely charged electrosomes coagulate, similarly charged stabilize. The valency rule holds. With weakly charged, strongly hydrated, isostable colloids such as gelatin, higher concns. of electrosomes are required to cause radical changes in state, the valency rule is not important and the *Hoffmeister series* is displayed. Although the H<sup>+</sup> concn. plays a very important part in the behavior of colloids it is not true that the Hoffmeister series disappears

when the  $\phi_H$  of the sol is kept const. The Hoffmeister series is observed in numerous phenomena of pure salt solns., for example the hydration of ions, their mobility, the surface tension, and the position in the electromotive series. F. L. BROWNE

**Dissolution processes in colloids.** N. P. PRISKOV. *Kolloid-Z.* 32, 24-8(1923).—The addition of gelatin enormously reduces the velocity of dissoln. of colloids by suitable reagents. Since gelatin does not affect the velocity of reactions between substances in true soln., this phenomenon furnishes a delicate *indicator for distinguishing between colloids and true solns.* Colloid reactions in which the effect was observed include soln. of colloidal Au or CuS by KCN and of  $As_2S_3$  by alkalies, conversion of colloidal  $As_2S_3$  to HgS by  $Hg(CN)_2$ , and the color changes in Congo red and fuchsin. An amicroscopic Au sol with particles  $1.86 \mu$  in size exhibits the effect as strongly as one with particles  $55 \mu$ , while a true soln. with mols. certainly  $0.46 \mu$  in diam. does not show any trace of the effect. This is proof that the difference between colloids and true solns. is qualitative as well as quant., the colloid systems having an interface at which adsorption effects come into play. The retardation of velocity in these reactions increases with the amt. of gelatin less rapidly than the concn. of gelatin, the curve resembling that of an adsorption process. All colloids require the presence of a third substance in true soln. for stability. The more of this stabilizer present the less marked is the influence of gelatin addn. because the opportunity for further surface effects is thereby diminished. F. L. BROWNE

**The transition from the colloidal to the crystalloidal state.** Solutions of potassium oleate. L. L. BIRCUMSHAW. *J. Chem. Soc.* 123, 91-7(1923).—The object of these studies is to discover whether the transition from the crystalloid to the colloid state of substances which are colloiddally dispersed in one solvent and mol. dispersed in another takes place gradually. Detns. were made of the d., viscosity, and surface tension of two complete series of mixts. from pure Et alc. to pure  $H_2O$ , each contg., resp., 1.0 g. and 3.2 g. K oleate per 100 cc. of solvent. The increase in d. of the solns. over that of the mixed solvent is practically const. up to about 45% alc., then rises rapidly up to 100% alc. The increase in viscosity over the mixed solvents falls rapidly up to 15% alc., then is const. up to 40% alc., falls to a min. at 80%, and rises again slightly up to 100%. The lowering of the surface tension falls off rapidly to zero beyond 45% alc. The results suggest that there are 3 stages in the breaking down of the colloidal aggregates, extending over the ranges 0-15, 15-45, and 45-100% alc. F. L. BROWNE

**Measurements of adsorption processes by means of the interferometer.** OTTOMAR WOLFF. *Kolloid-Z.* 32, 17-9(1923).—The accuracy and rapidity of the interferometer for detg. concns. of solns. either in absolute terms or relative to some standard recommend it for greater use by chemists. Descriptions are given of its use in detg. the adsorption of gelatin by charcoal, kaolin, kieselguhr, etc., and in controlling the purification of solns. by adsorbents in the factory. F. L. BROWNE

**Negative adsorption.** II. Calculation of the amount of solute taken up. M. A. RAKUZIN AND T. GÖNKE. *Biochem. Z.* 132, 82-3(1922); cf. *C. A.* 16, 3017.—An adaptation of Curvich's formula for positive adsorption (*C. A.* 8, 2090). F. S. H.

**Physico-chemical attractive force.** II. The theory of adsorption. I. GURVICH. *Kolloid-Z.* 32, 80-91(1923).—Continuing the work already reported (*C. A.* 8, 2090; 9, 3003, 3005) G. considers the heat of wetting as a function of the attractive force between adsorbent and adsorbed substance. By comparing the heat of wetting and adsorption by floridin, clay, and charcoal, of various org. compds. and  $H_2O$  he finds that O compds. have a greater heat of wetting with, and are also adsorbed more by, adsorbents contg. O compds. or are "oxophil," while hydrocarbon compds. are more attracted by charcoal or are "carbophil." With increase in mol. wt. of a series, the oxophil effect of O decreases to a min. at about  $C_8$ ; the attractive force increases again because of increase in mol.

wt. Degree of pulverization of floridin is also a measure of attractive force. In adsorption from soln. both solute and solvent mols. are attracted; positive or negative adsorption depends on concn. and on relative affinities of two mols. for the adsorbent. The quantity adsorbed from soln. of a substance is inversely proportional to the heat of wetting of the solvent with the adsorbent. Contrary to Freundlich's ideas adsorption of  $C_6H_5COOH$  from org. solvents by floridin or of paraffin by charcoal is rather high. In regard to adsorption from soln. mols. of solute adsorbed lower the attractive force of adsorbent for other mols. of the same compd. but increase it for mols. of solute, so that in adsorption of mixts. there is greater adsorption of both than when adsorbed separately. The idea of this attractive force is also applied to solvation, and the advantages of this idea over the Freundlich-Gibbs adsorption theory in predicting results are pointed out.

BENJAMIN S. NEUHAUSEN

Remarks on "General theory of adsorption in solution" of Wo. Ostwald and R. de Izaguirre. B. GUSTAV. *Kolloid-Z.* 31, 358-62(1922).—A discussion of presumed erroneous interpretations of mathematical terms and criticisms of the interpretations of the exptl. data of A. M. Williams and B. Gustafson (now Gustaver). A. M.

The general theory of adsorption from solutions. WOLFGANG OSTWALD AND RAMON DE IZAGUIRRE. *Kolloid-Z.* 32, 57-64(1923); cf. *C. A.* 16, 2627.—Polemical with Br. Gustaver (preceding abstract). The authors admit having confused the quantities  $n$  and  $n_0$  (actual and apparent adsorption) in their references to the work of A. M. Williams, as other writers have also done in consequence of lack of clearness in W.'s work. However, G.'s assertion that their equations lead to the same conclusions as W.'s is refuted. Mention is made of the necessity of distinguishing between absolute and relative layer-thicknesses for the adsorption layers. In the adsorption of colloid particles the adsorption layer in absolute measure is obviously not monomolecular, but at best monomolecular. The thickness of the adsorbed layer will vary with the size of particles of the adsorbed material and the amt. of solvent adsorbed with it. G.'s assumption that the adsorbed layer is only monomolecular in thickness is refuted by the direct ultramicroscopic observations of the adsorbed layers of surface active emulsoids by Traube and Klein (*C. A.* 15, 3685) who found thicknesses up to 0.1 mm. In view of the disintegration theory set forth previously as well as in consideration of the manifold nature of adsorption potentials it does not seem possible to give a general answer to the question of *thickness of adsorbed layers*.

F. L. BROWNE

Adhesion pressure, surface activity, and the tendency to formation of submicrons. I. TRAUBE. *Kolloid-Z.* 32, 22-4(1923); cf. *C. A.* 3, 1485; 5, 613, 3077.—Salts of the alkaloids are molecularly dispersed in  $H_2O$ , have in consequence of their ionic charge a large adhesion pressure (Haftdruck), and as a result of this are surface-inactive and do not form submicron aggregates. The uncharged alkaloid particles formed on addn. of bases to the alkaloid salts, have usually a very slight adhesion pressure, are surface active, and form submicrons. The adhesion pressure is less the greater the mol. wt. Similar considerations hold for the fatty acids. Addn. of  $HCl$  gives the free acids with low adhesion pressure, high surface activity and submicron formation. A close relation exists between adhesion pressure and soly. Substances like carbohydrates and alkyl halides which are only slightly sol. in  $H_2O$  have a low adhesion pressure and are dispersed as submicrons. More sol. materials, as amyl alc., phenol, and aniline, have a larger adhesion pressure and their concd. solns. have submicrons and mol. dispersed particles and are surface-active. Sol. substances, as glycerol, have a large adhesion pressure, are surface-inactive and give no submicrons. For suspensoid substances, as Au, which do not influence the surface tension of  $H_2O$ , the relation between adhesion pressure and surface activity does not hold.

F. L. BROWNE

Forces of adhesion in solutions. Experimental studies on coarse suspensions.



S. WOSNESSENSKY. *Kolloid-Z.* 31, 333-8(1922).—Coarse suspensions (size about  $5\mu$ ) were prepd. by agitating various substances with  $H_2O$ . After 2 min. standing, 10 cc. were mixed with electrolyte in a glass cylinder and the time was observed when a certain clearing had taken place. Kaolin, carbon, kieselguhr,  $Sb_2S_3$ ,  $SnS_2$ ,  $Sb_2O_3$ ,  $Sb_2S_5$ , and molybdic acid as negative, and  $Al_2O_3$ ,  $Fe_2O_3$ ,  $NiO$ ,  $SnO_2$  and  $Sb_2O_4$  as positive suspensions were examd. The results (given in tables and curves) show that pptn. by and adsorption of electrolyte run parallel.

A. MUTSCHILLER

Solubility. VIII. Solubility relations of certain gases. N. W. TAYLOR AND J. H. HILDEBRAND. *J. Am. Chem. Soc.* 45, 682-94(1923); cf. *C. A.* 16, 518.—Measurements have been made of the soly. of Cl in  $C_2H_6$ ,  $CCl_4$ ,  $SiCl_4$  and  $C_6H_6Br_2$ . Soly. data for various gases are summarized and their theoretical relations discussed.

H. JERMAIN CREIGHTON

Theory of solubility. J. H. HILDEBRAND. *Phys. Rev.* 21, 46-52(1923).—Restatement of H.'s theory of soly. as given in a series of papers (*C. A.* 10, 2426; 11, 3146; 13, 1663; 15, 6, 1245; 16, 518).

JAMES M. BELL

The solubility of copper hydroxide in sodium hydroxide solution. G. SVENSEN MELBYR. *Medd. Vetenskapsakad. Nobelinst.* 4, No. 8, 11 pp.(1922).—The fact that within certain limits the soly. is approx. a straight-line function of the NaOH concn. indicates that the soln. is a true one and not colloidal. Based on equiv. concns., the soly. curve of the unstable  $Cu(OH)_2$  for the interval 2.65-6.60 *N* NaOH was found to be:  $Cu(OH)_2 = 0.0450 NaOH - 0.095$ . Assuming that the unstable Cu hydroxide occurs in the form of  $H_2Cu_2O_3$  and in soln. as  $Na_2Cu_2O_3$ , calcs. show that  $K_1/K_{H_2O} = 0.0020$  at  $22^\circ$  and therefore that  $K_1 = 0.9 \times 10^{-17}$ . For the stable form  $H_4CuO_4$ ,  $K_1/K_{H_2O} = 0.00029$  and  $K_2 = 1.3 \times 10^{-13}$  at  $22^\circ$ . From an unstable, satd., filtered soln.  $CuO$  sepd. after some time.

C. C. DAVIS

The law of solution. PAUL MONDAIN-MONVAL. *Compt. rend.* 176, 301-4(1923).—In order to test the applicability of the equation,  $500 L (dT/T^2) + i (dC/C) = 0$  for very sol. salts the value of the heat of soln. (*L*) for  $NaNO_3$  was calcd. from soly. measurements at 16, 20 and  $25^\circ$  to be  $-2160$  cal. This value agrees well with a calorimetric value of  $-2130$  cal. and an indirectly detd. value of  $-2150$  cal. J. A. ALMQUIST

Anomalous osmose of solutions of electrolytes with collodion membranes. I. Electric properties of the membrane system. F. E. BARTELL AND D. C. CARPENTER. *J. Phys. Chem.* 27, 101-16(1923).—A method for prepg. flat collodion membranes is described, as well as a two-compartment cell used for the measurements. Osmose values have been obtained for 13 different salts, an acid and a base, each at 4 different concns. The curves almost all exhibit sharp breaks and sometimes even minimum points. The p. d. of the two sides of the membrane has been measured for each soln. The sign of the charge upon the membrane has been detd. by cataphoresis. Upon the result of this expt. is based an explanation for the very low and even negative osmotic values obtained with certain salts.

C. R. PARK

A low-temperature electrolyte. W. H. RODERUSH AND T. O. NYTEMA. *J. Am. Chem. Soc.* 45, 332-7(1923).—Mixts. of NO and HCl condense at temps. of 120 to  $130^\circ K$ . forming a deep blue liquid contg. a complex of the probable compn.  $NOHCl$ . The soln. has a max. cond. greater than  $10^{-3}$  mhos.

C. R. PARK

The electrolytic dissociation of dibasic acids. I. The determination of the second dissociation constants of some acids from electrometric measurements. ERIK LARSSON. *Z. anorg. allgem. Chem.* 125, 281-94(1923).—The theory of Bjerrum for ionic equil. (*C. A.* 13, 1174) is applied to solns. contg. a dibasic acid and the neutral salt. A relation is worked out by means of which the second dissociation const.  $K_2$  can be calcd. from measurements of the  $H^+$  activity in a series of these soln. The  $H^+$  activity was detd. by means of a quinhydrone electrode. The following values of  $K_2$  ( $\times 10^{-6}$ ) were calcd.

for 18°: succinic acid 2.4, pyrotartaric acid 2.3, *l*-malic acid 7.8, *d*-tartaric acid 41, fumaric acid 34, thiodiglycolic acid 35.

J. A. ALMQUIST

The ionization of water in solutions of electrolytes. E. DOUMER. *Bull. soc. chim.* 33, 49-55(1923).—During electrolysis of HCl solns.  $O_2$  is evolved at the anode as well as  $Cl_2$ . This is not due to a secondary reaction between nascent  $Cl$  and  $H_2O$  because no  $O_2$  is evolved when neutral chlorides are used. Assuming that the vols. of  $O_2$  and  $H_2$  evolved are measures, resp., of the no. of mols. of  $H_2O$  and of the sum of the  $H_2O$  and HCl mols. which are ionized in the soln., measurements with HCl solns. varying from 1.25 to 55.8 g. per l. and with c. ds. varying 40-fold, show that 2 mols. of  $H_2O$  are ionized for every mol. of HCl. Measurements of the change in concn. of HCl in the anode and cathode compartments show that only  $1/3$  the total amt. of electricity passing through the soln. is used up in decomposing HCl. This is considered an independent confirmation of the above conclusion. The theory that there are 2 mols. of ionized  $H_2O$  present for every mol. of ionized HCl is offered as the explanation of the fact that the mol. cond. of acid solns. is much greater than that of neutral salt soln. of the same concn.

F. L. BROWNE

The hydration of the lithium ion. J. BABOROVSKY AND J. VELISEK. *Chem. Listy* 16, 250-6(1922).—A new app. suitable for detg. the transport numbers and hydration of ions consists of two membranes of parchment paper sepg. the central portion of the soln. from the anodic and cathodic portions and also of an arrangement whereby the anodic and cathodic vessels can be disconnected and weighed with their contents. The hydration of the Li ion was calcd. from the change in wts. and in concns. of the solns. around the electrodes. The detn. of the hydration of ions by this method is complicated by electroosmosis. This has been measured by replacing the two parchment paper membranes by a single membrane and estg. the differences in the concn. and sp. gr. of the central portion after each expt. The Li ion has one more mol. of water of hydration than the Cl ion. The transport number of Li in a decinormal soln. of its chloride is  $.3128 \pm 0.0048$ . The hydration of ions should be expressed in terms relative to that of the H ion (the most mobile of all), which would be put equal to zero.

J. C. S.

Hydration of acetic acid and hydrochloric acid and the factors determining the activity of the hydrogen ion. W. C. M. LEWIS, D. E. MERRIMAN AND T. MORAN. *J. Am. Chem. Soc.* 45, 702-12(1923); cf. *C. A.* 16, 4116.—The activity of  $H^+$  (produced from AcOH) in the presence of various amts. of  $C_{12}H_{22}O_{11}$  has been detd. at 30°. The activity of  $H^+$  can be accounted for on the assumption that each mol. of AcOH is hydrated to the extent of 3 mols.  $H_2O$ , and then identifying the activity with the concn. of the  $H^+$  per unit of free  $H_2O$  space in the  $C_{12}H_{22}O_{11}$  soln. By combining a space correction with the heat of diln. of the ion, it is possible to account for 80 to 90% of the observed activity of the  $H^+$  produced from HCl. The av. degree of hydration of HCl in soln. between 0.1 and 1.2 *N* is approx. 7.

H. JERMAIN CREIGHTON

Hydrolysis of glycylglycine by hydrochloric acid. IV. S. LAICHNIKOV. *J. Russ. Phys. Chem. Soc.* 52, 147-50(1920).—Both at 10° and 100°, the hydrolysis of glycylglycine by means of HCl proceeds, for about  $1/3$  of its course, in accordance with the equation for a reaction of the first order (cf. Euler, *C. A.* 1, 1742).

J. C. S.

Statistical theory of monomolecular reactions. W. H. RODRIGUEZ. *J. Am. Chem. Soc.* 45, 806-14(1923).—An equation for the rate of a monomol. reaction has been derived from the kinetic theory.

H. JERMAIN CREIGHTON

Velocity of reaction in mixed solvents. IV. Influence of the base on the velocity of saponification of esters. A. E. CASHMORE, H. MCCOMBIE AND H. A. SCARBOROUGH. *J. Chem. Soc.* 123, 197-207(1923); cf. *C. A.* 16, 1527.—The reaction between Et esters of certain monobasic acids and certain hydroxides in aq. alc. is of the 2nd order and independent of the concns. Under the same conditions the velocity of the reaction

decreases as the base is changed in the following order:  $\text{Ba(OH)}_2$ ,  $\text{KOH}$ ,  $\text{LiOH}$ ,  $\text{Me}_2\text{NOH}$ . The velocities appear to be some function of the relative strengths of the bases and their power to form ethoxides. The curve exhibiting the relation between the velocity const. and the compn. of the solvent shows certain common characteristics for all the bases examd.

H. JERMAIN CREIGHTON

**Catalyzers and chemical equilibrium.** Reply to a note by J. F. Durand. J. CLARENS. *Bull. soc. chim.* 33, 43-8(1923).—Polemical, cf. C. A. 16, 2440; 17, 16.

F. L. BROWNE

**The activation of oxygen and hydrogen peroxide by hydrogenized palladium.** N. D. ZELINSKII AND P. P. BORISSOV. *Ber.* 56B, 396-406(1923).—If air is led into 10 cc. of a soln. contg. 2 drops 10%  $\text{H}_2\text{SO}_4$ , 0.3 cc. 0.01% indigo soln., and a piece of hydrogenized Pd foil (Pd-H), the indigo is decolorized by oxidation in 45-50 min., or without acid, in 15 min. There is formed in such a system 0.1 g. per l. of  $\text{H}_2\text{O}_2$ , but this concn. of  $\text{H}_2\text{O}_2$ , alone, requires 6-7 hrs. to decolorize the indigo. Bach (*Ber.* 33, 1097(1900)) attributed the catalytic effect to the formation of hydrogen tetroxide. However, the above system, (Pd-H) +  $\text{H}_2\text{O}$  + air, may be replaced by the system, (Pd-H) +  $\text{H}_2\text{O}_2$  +  $\text{CO}_2$ -gas, with identical results. Therefore, the air merely aids in the formation of  $\text{H}_2\text{O}_2$ , which, in the presence of Pd-H, oxidizes the indigo. Also, the formation of Bach's *hydrogen tetroxide* is precluded. When Pd-H acts separately on  $\text{H}_2\text{O}_2$  or indigo, reduction occurs, but it is shown that its action on a mixt. of them is an oxidation of the indigo. If  $\text{CO}_2$  is led into a 0.4 g. per l.  $\text{H}_2\text{O}_2$  soln., contg. Pd-H, until the concn. falls to 0.1 g. per l., the resulting soln. decolorizes indigo soln. in 2 hrs. instead of 6-7 hrs. required by the same concn. of  $\text{H}_2\text{O}_2$  alone. If  $\text{CO}_2$  is led into the phase, (Pd-H) +  $\text{H}_2\text{O}_2$  soln., until the  $\text{H}_2\text{O}_2$  is completely reduced, the soln. shows no oxidizing action. But, if to this soln. there is added some 0.1 g. per l.  $\text{H}_2\text{O}_2$  soln., the  $\text{H}_2\text{O}_2$  becomes activated and decolorizes indigo soln. in 2 hrs. instead of 7 hrs. in its unactivated condition. Therefore, there are formed from  $\text{H}_2\text{O}_2$ , in the presence of Pd-H, very small quantities of a substance which exercises an activating action on the oxidation of indigo by  $\text{H}_2\text{O}_2$ . The activating liquid is formed also when Pd-H and  $\text{H}_2\text{O}_2$  soln. stand together several hrs. Neither Pd +  $\text{H}_2\text{O}$  nor (Pd-H) +  $\text{H}_2\text{O}$  gives an activating soln. Traces of Pd were not detected in the activating liquid. The activating substance has the character of an *inorganic peroxidase*.

R. H. LOMBARD

**The phenomenon of molecular association.** ETTORÉ CARDOSO AND GABRIELE BATTISTA. *Anales soc. españ. fis. quim.* 20, 420-32(1922).—A general discussion, largely mathematical. No exptl. data are given.

L. E. GILSON

**Dissociation of molecular hydrogen, from the entropies of diatomic and monatomic hydrogen.** GRAHAM EDGAR. *J. Am. Chem. Soc.* 45, 673-6(1923).—The free energy of dissoc., the dissoc. const., and the degree of dissoc. of mol. H into at. H have been calcd. from the entropies of the substances and published data for the heat of dissoc. The results indicate in accordance with the conclusions of Duffenbach (C. A. 16, 1701; 17, 924) and of Saha (C. A. 15, 468) that H is much more highly dissociated at high temps. than earlier calcs. had indicated.

JAMES M. BELL

**Topochemical reactions: homologous and substituted structural forms.** V. KOHL-SCHÜTTER AND VL. SEDELINOVICH. *Z. Elektrochem.* 29, 30-44(1923); cf. C. A. 17, 1361.—Electrolytically prepd.  $\text{Cu(OH)}_2$  has been studied, in order to det. under what circumstances definite structural forms are obtained in topochem. reactions. By varying the c. d. and the bath concn. different structural forms of  $\text{Cu(OH)}_2$  were obtained. The following topochem. reactions with  $\text{Cu(OH)}_2$ , which immediately yield solid substances, were employed: (a) spontaneous formation of the oxide; (b) the formation of  $\text{CuS}$  with  $\text{H}_2\text{S}$  and the change of the former to  $\text{Cu}_2\text{S}$ ; (c) the action of  $\text{H}_2\text{O}_2$  with the formation of  $\text{CuO}$ ; (d) reduction to  $\text{Cu}_2\text{O}$  with hydrazine; (e) the formation

of basic salts by means of concd. KCl solns. Differences in the structural form of  $\text{Cu}(\text{OH})_2$  were judged according to the velocity of its transformation into the oxide, and according to the behavior of its suspensions. The velocity of sedimentation also was used to investigate the products formed in reactions (b), (c), (d) and (e), and the velocities of these reactions were used as a basis for the comparison of the different forms of  $\text{Cu}(\text{OH})_2$ . A clear connection exists between the structural form of the  $\text{Cu}(\text{OH})_2$  on the one hand, and the progress of the reactions (a), (b), (c), (d) and (e) and the form of the resulting product on the other. The structural form of  $\text{Cu}(\text{OH})_2$  depends to a large extent on the velocity of its formation.

II. JERMAIN CRRIGHTON

**Problem in thermometry.** S. P. OWEN. *Proc. Univ. Durham Phil. Soc.* **6**, Pt. III, 148-59(1922).—Mathematical. A soln. to the problem of obtaining temps. from readings of a thermometer placed in a medium whose temp. is changing: taking into consideration the contg. vessel but neglecting convection in the liquid. There are solns. for the four cases: (a) spherical bulbs with (1) infinite surface cond., (2) finite surface cond.; (b) cylindrical bulbs with (3) infinite and (4) finite surface cond. A. E. S.

**Variation of diathermancy with the temperature of the radiating source.** S. LEROY BROWN. *Phys. Rev.* **21**, 103-6(1923).—A table gives the percentage of the total radiation transmitted through water, ice, rock salt, white mica and glass. The source was a tubular elec. furnace. The radiation was focussed by a mirror on a thin piece of  $\text{CuO}$  of 1 sq. mm. area and of 10,000 ohms resistance with a temp. coeff. of resistance of 0.01 per degree. This is simple to construct and is sensitive to 1% of radiation from a tubular elec. furnace at  $500^\circ$ .

A. E. STEARN

**Adiabatic condensation of ether vapor.** A. I. CLARK. *Trans. Roy. Canadian Inst.* **13**, 93-7(1921).—For an adiabatic expansion  $dx/dT = L/hv(1-x)/c$ , where  $x$  is the dryness or fraction of the mass which is vapor,  $h$  the sp. heat of the satd. vapor,  $c$  that of the liquid,  $L$  the latent heat of vaporisation and  $T$  the temp. If  $h$  be positive,  $dx$  is positive or the mixt. becomes dryer when expanded, while if  $h$  be negative, the mixt. becomes wetter on expansion (condensation takes place). If  $x$  is near unity, a negative value of  $h$  always means condensation with expansion. The condensation of  $\text{Et}_2\text{O}$  vapor near the crit. temp. may be regarded, therefore, as proof that the sp. heat of  $\text{Et}_2\text{O}$  vapor is negative.

H. JERMAIN CREIGHTON

**Studies on specific heats. III. Specific heat of isomeric compounds and aromatic hydrocarbons in the solid state.** M. PADOA. *Gazz. chim. ital.* **52**, II, 202-7(1922).—In Paper I (*C. A.* **15**, 1844) P. showed that isomers in the solid state have a different sp. heat which was attributed to the difference in no., energy and disposition of the bonds. These preliminary results are confirmed by the results here described in which the sp. heat of various groups of isomeric compds. were compared. The sp. heats of isomers in the solid state are often different and are sometimes less for those that contain large amts. of energy. For fumaric and maleic acids the curves representing the change of sp. heat with the temp. intersect at  $14^\circ$ , from which a reversal of the relative stability of these compds. with increase in the temp. is predicted. The sp. heats of optical antipodes are identical. The mean atomic heat in a series of polynuclear benzene hydrocarbons varies and the difference observed is increased by a different disposition of the bonds in the mol. and in the crystals. The mean atomic heat in the isomorphous compds. *anthracene* and *phenanthrene* is the same and therefore the no., direction and energy of the bonds are the same.

E. J. WITZEMANN

**The dissociation of potassium chloroiridate.** G. GIRE. *Compt. rend.* **176**, 241-4(1923).—G. has followed the thermal decomp. of  $\text{K}_3\text{IrCl}_6$  between the temp.  $574$ – $844^\circ$  by measuring the tension of the evolved Cl. From the values thus obtained, it was possible to compute the heat of dissociation of this compd. and also, the heat of fusion of KCl.

L. T. FAIRHALL

**The dissociation of silver sulfate.** G. MARCHAL. *Compt. rend.* 176, 299-301 (1923).—The thermal decompn. of  $\text{Ag}_2\text{SO}_4$  according to the equation  $\text{Ag}_2\text{SO}_4 (\text{liq.}) = 2\text{Ag} (\text{solid}) + \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g})$  involves also the equil.  $2\text{SO}_2 (\text{g}) = 2\text{SO}_3 (\text{g}) + \text{O}_2 (\text{g})$ . The decompn. pressure of  $\text{Ag}_2\text{SO}_4$  was measured at temps. between  $820^\circ$  and  $1220^\circ$  and the partial pressures of  $\text{SO}_2$ ,  $\text{SO}_3$  and  $\text{O}_2$  were calcd. from the known values of the  $\text{SO}_2$  equil. (cf. Bodenstein and Pohl, *Z. Elektrochem.* 11, 373(1905)). At  $820^\circ$   $\text{Ag}_2\text{SO}_4$  and Ag are in equil. with 5 mm.  $\text{SO}_2$ , 6.9 mm.  $\text{SO}_3$  and 7.2 mm.  $\text{O}_2$ ; at  $1220^\circ$  with 59.6 mm.  $\text{SO}_2$ , 1075.7 mm.  $\text{SO}_3$  and 1110.6 mm.  $\text{O}_2$ . The heat absorbed during the decompn. of  $\text{Ag}_2\text{SO}_4$  is calcd. to be 97800 cal. at ordinary temp. J. A. ALMQUIST

**Vapor pressures of certain hydrated metal sulfates.** C. D. CARPENTER AND E. R. JERRY. *J. Am. Chem. Soc.* 45, 578-90(1923).—The vapor pressures of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$  and of satd. solns. of these salts have been detd. by the static method at various temps. between  $25^\circ$  and  $100^\circ$ . A new transition point has been located for  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  at  $45.1^\circ$  and for  $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$  at  $41.5^\circ$ , while the value of that for  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} - 6\text{H}_2\text{O}$  has been detd. more exactly at  $48.4^\circ$ . H. JERMAIN CRRIGHTON

**Determination of the dissociation pressures of hydrated salts by a dynamical method.** II. J. R. PARTINGTON AND D. B. HUNTINGFORD. *J. Chem. Soc.* 123, 160-70 (1923).—The disson. pressures have been measured by a dynamical method (without the use of glass wool) similar to that previously employed (cf. C. A. 5, 2357), and the following values (mm. Hg) obtained, resp., at  $25^\circ$ ,  $30^\circ$  and  $35^\circ$ :  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , 7.92, 11.74, 17.01;  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O} \rightarrow \text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , 11.10, 15.25, 20.74. The heats of hydration calcd. from these data are 3460 and 930 cal., resp. H. JERMAIN CRRIGHTON

**Phase relations in the system, sodium amide-potassium amide, as determined from melting-point curves.** C. A. KRAUS AND E. J. CUY. *J. Am. Chem. Soc.* 45, 712-5 (1923).—The existence of a compd.,  $\text{NaNH}_2 \cdot 2\text{KNH}_2$  is indicated, having a transition point at  $120^\circ$ . An eutectic between the compd. and  $\text{NaNH}_2$  occurs at a compn. of 33 mol. % of K and a temp. of  $92^\circ$ . H. C. PARKER

**Realization of perpetual motion of the second kind.** N. V. KARPEN. *Bull. sci. acad. Roumaine* 8, 27-31(1922-23).—Various thermoelec. cells can be formed of two immiscible liquids, directly superposed, in which is dissolved (or in colloidal soln.) a salt or a mixt. of salts of a given metal, each liquid being in contact with an electrode of this same metal. The operation of these cells does not seem to produce any chem. reaction or any change in the concn. of the two solns. Examples are given of  $\text{ZnSO}_4$  in  $\text{H}_2\text{O}$  and Am alc., and of peptonate of Fe in  $\text{H}_2\text{O}$  and Am alc. (in continuous operation since Dec. 5, 1921). The energy developed so far in these cells is of the order of a few microwatts per cc. capacity. A. P.-C.

**Physical constants and ultimate rational units.** G. N. LEWIS. *Phil. Mag.* 45, 266-75(1923).—After reviewing the fundamental relations of phys. units and constns. and the desirability of choosing them so as to eliminate as many as possible and to reduce the remaining ones to the most rational basis, the previous efforts to this end are critically discussed. The ultimate rational unit (U. R. U.) chosen by Lewis and Adams (*Phys. Rev.* 3, 92(1914)) is  $(4\pi e)^2$ , where  $e$  is the charge of an electron.  $(4\pi e)^2$  has the dimensions of energy  $\times$  length; hence the new unit of energy or mass is the reciprocal cm.  $1 \text{ erg} = 2.779 \times 10^{18} (1/\text{cm.})$  and  $1 \text{ g.} = 2.449 \times 10^{22} (1/\text{cm.})$ . Energy and mass thus acquire the dimensions of curvature or frequency or acceleration, and all phys. quantities are reduced to the dimensions of a power of length. The successful prediction of the values of constns. by means of U. R. U.'s illustrates their utility. Assuming that the const.  $a$  of Stefan's law  $E/V = aT^4$  would become unity if the other quantities were expressed in U. R. U.'s, a value in ordinary units of  $(ac/4) \times 10^8$  was predicted

as 5.70, which at that time was within 0.03 of only one out of 7 values of different authorities and differed by 0.11 from the av. of all. The latest value (of Coblenz) is  $5.72 \pm 0.012$ . Planck's const.  $h$  was predicted in ordinary units as  $6.560 \times 10^{-27}$  when the accepted value was  $6.615 \times 10^{-27}$ . The present accepted value is  $6.557 \times 10^{-27}$ . The entropy of 4 monat. gases has been calcd. and compared with exptl. values as follows: He, exptl. 29.2, calcd. 29.8; A 36.4 and 36.7; Cd 40.0 and 39.8; Hg 41.3 and 41.5, resp. Tolman's principle of similitude (C. A. 14, 2110) extends the idea to the general assumption that all new fundamental const. will be found to be dimensionless in U. R. U.'s. Rydberg's const.  $h\nu$  is an exception, but the choice of  $h\nu$  as the unit of energy is deferred for the present. An editorial note appended by Sir Oliver Lodge expresses doubt as to the utility of U. R. U.'s or of any attempt to unify essentially different phys. quantities.

S. C. LIND

The hydrogen electrode and some of its applications. S. W. PENNYCUICK. *Chem. Eng. Mining Rev.* 15, 124-6 (1922).—A general resumé.

C. C. DAVIS

Determination of chemical equilibrium between different oxidation stages by electromotive force measurements. I. Equilibria between the sulfates of bivalent, trivalent and quadrivalent manganese in sulfuric acid solution. G. GRUBE AND K. HUBBRICH. *Z. Elektrochem.* 29, 8-17 (1923).—Measurements have been made at 15° in a soln. contg. 0.05 g.-atom of Mn (in the form of  $\text{MnSO}_4$ ) of the normal potential of the several oxidation stages for the concn. ratio 1:1. The potential  $E_{\text{Mn}^{++}} \rightarrow \text{Mn}^{+++} = +1.511$  v.,  $E_{\text{Mn}^{+++}} \rightarrow \text{Mn}^{++++} = +1.642$  v., and the potential  $E_{\text{Mn}^{++++}} \rightarrow \text{Mn}^{++++} = +1.577$  v. These potentials depend somewhat on the total concn. of the Mn and markedly on the acid concn. With increase in the latter the potentials change to higher positive values. By means of the measured potentials, the equil. const. of the reaction  $\text{Mn}_2(\text{SO}_4)_3 \rightleftharpoons \text{MnSO}_4 + \text{Mn}(\text{SO}_4)_2$  has been calcd. The value of this const. varies with the total Mn concn. and the concn. of the acid. With increase in the latter the position of equil. is displaced towards the left. The existence of this equil. is the cause of the abnormal hydrolytic behavior of  $\text{Mn}_2(\text{SO}_4)_3$ . Hydrolysis converts this compd. into  $\text{MnSO}_4$  and a ppt. of hydrated  $\text{MnO}_2$ , owing to the hydrolytic decompn. of the  $\text{Mn}(\text{SO}_4)_2$  resulting as shown in the above equation. This causes the reaction to proceed completely from left to right.

H. JERMAIN CARRINGTON

Condition of bismuth salts in aqueous solutions and the molal electrode potential of bismuth. D. F. SMITH. *J. Am. Chem. Soc.* 45, 360-70 (1923).—Cond. measurements carried out upon solns. of  $\text{Bi}(\text{NO}_3)_3$  in various concns. of  $\text{HNO}_3$  indicate that the Bi exists largely in the form of partially ionized  $\text{Bi}(\text{NO}_3)_3$ . Soly. measurements point to the same conclusion. Cond. measurements with solns. of  $\text{Bi}(\text{ClO}_4)_3$  in excess  $\text{HClO}_4$  show that  $\text{Bi}(\text{OH})_3 + \text{ClO}_4^-$  has the cond. of a uni-univalent salt. The basic salt corresponding to this formula is stable even in the presence of a moderate excess of  $\text{HClO}_4$ , changing slowly to  $\text{BiOH}(\text{ClO}_4)$  on the addition of excess acid. E. m. f. measurements have been made upon solns. of bismuth perchlorate. The following molal potentials were calcd. upon the assumptions that Bi exists in soln. wholly in the form of (1) the ion  $\text{BiO}^+$ , and (2) the ion  $\text{Bi}(\text{OH})^{++}$ ; (1)  $\text{Bi}(s)$ ,  $\text{BiO}^+ + \text{H}^+$ , 0.314 v.; (2)  $\text{Bi}(s)$ ,  $\text{BiOH}^{++} + \text{H}^+$ , 0.298 v.

C. R. PARK

Electrode potential of bismuth determined by equilibrium measurements. ERNEST H. SWIFT. *J. Am. Chem. Soc.* 45, 371-7 (1923); cf. preceding abstract.—Measurements have been made at 25° of the equil. conditions in  $\text{HClO}_4$  soln. of the reaction  $3\text{Cu}(s) + 2\text{Bi}(\text{ClO}_4)_3 = 2\text{Bi}(s) + 3\text{Cu}(\text{ClO}_4)_2$ . Values of the electrode potential of Bi have been calcd. under the assumptions that Bi in the soln. exists wholly in the form of (1) the ion  $\text{BiO}^+$  (2) the ion  $\text{BiOH}^{++}$  as follows: (1)  $\text{Bi}(s)$ ,  $\text{BiO}^+ + \text{H}^+$ , 0.318 v.; (2)  $\text{Bi}(s)$ ,  $\text{BiOH}^{++} + \text{H}^+$ , 0.310 v.

C. R. PARK

The electromotive behavior of some binary alloys. VI. The electromotive be-

havior of alloys of sodium with lead, thallium, zinc and cadmium. R. KREMANN AND PETER VON REININGSHAUS. *Z. Metallkunde* 12, 273-87(1920); cf. *C. A.* 15, 2771.—By the Poggendorf compensation method, the e. m. f. in v. of certain cells with Pb, Tl, Zn and Cd was measured. For the cell  $\text{Pb} | 0.1 \text{ N NaI} | \text{Pb}_2\text{Na}_{(1-x)}$  in  $\text{C}_2\text{H}_5\text{N}$  and in  $\text{H}_2\text{O}$  the potential of pure Na was 1.835-1.847v. From 0 to 20% Pb the potential was virtually that of pure Na. The values decreased with several sudden drops to 0 at 100% Pb, and the curve was in general similar to that of Mathewson (*Z. angew. Chem.* 50, 175(1908)). From 70 to 100% Pb the values were also detd. by the cell  $\text{Pb} | \text{N NaSO}_4 | \text{Pb}_2\text{Na}_{(1-x)}$  in  $\text{H}_2\text{O}$ . Of the 4 compds. of Na with Pb,  $\text{Na}_4\text{Pb}$  and  $\text{Na}_5\text{Pb}$  could not be definitely distinguished by their potentials. The first is approx. 300, the other 350 milliv. "nobler" than Na.  $\text{NaPb}$  is 650,  $\text{Na}_3\text{Pb}$  1500 milliv. "nobler" than Na. For the cell  $\text{Tl} | 0.1 \text{ N NaI} | \text{Tl}_{(1-x)}\text{Na}_x$  in  $\text{C}_2\text{H}_5\text{N}$  and in  $\text{H}_2\text{O}$  the potential of pure Na was 1.504-1.551 v. From 50 to 100% Tl the cell  $\text{Tl} | 1 \text{ N Na}_2\text{SO}_4 | \text{Tl}_{(1-x)}\text{Na}_x$  in  $\text{H}_2\text{O}$  was used also. The values were approx. const. from 0 to 50% Tl at 1550 milliv., then taking a large and sudden drop to 1100 in  $\text{H}_2\text{O}$ , to 800 in  $\text{C}_2\text{H}_5\text{N}$ . A second drop to 40 at 75% Tl occurred, with subsequent decrease to 0 at 100% Tl. The compd.  $\text{TlNa}$  is assumed with a potential 1100 milliv. less "noble" than Tl and 480 milliv. "nobler" than Na. No evidence was obtained of the existence of  $\text{Na}_2\text{Tl}$  or  $\text{Na}_3\text{Tl}$ . For the cell  $\text{Zn} | 0.1 \text{ N NaI} | \text{Na}_{(1-x)}\text{Zn}_x$  in  $\text{C}_2\text{H}_5\text{N}$  the potential of pure Na was 1.424-1.454 v. From 85 to 100% Zn the cell  $\text{Zn} | \text{N Na}_2\text{SO}_4 | \text{Na}_{(1-x)}\text{Zn}_x$  in  $\text{H}_2\text{O}$  was also used. From 0 to 90% Zn the potential was virtually that of pure Na. At 90% it took a great drop of 1050 milliv. and then became approx. const. from 92 to 98% Zn at 400 milliv. The compd.  $\text{NaZn}_2$  is assumed, with a potential 1050 milliv. "nobler" than Na and 400 milliv. less "noble" than Zn. For the cell  $\text{Cd} | \text{N NaI} | \text{Cd}_x\text{Na}_{(1-x)}$  in  $\text{C}_2\text{H}_5\text{N}$  the potential of pure Na was 1.534-1.555 v. From 60 to 100% Cd the cell  $\text{Cd} | \text{N Na}_2\text{SO}_4 | \text{Cd}_x\text{Na}_{(1-x)}$  in  $\text{H}_2\text{O}$  was also used. From 0 to 66% of Cd the potential was virtually that of pure Na. At 66% it took a drop of 1300 milliv. and then remained const. to 80-85%, followed by a new drop of 150 milliv. This potential, 150 "nobler" than pure Cd, remained const. to 100% Cd. The compds.  $\text{NaCd}_2$  and  $\text{NaCd}_3$  are assumed. The potential of  $\text{NaCd}_2$  is 1300 milliv., of  $\text{NaCd}_3$  1450 "nobler" than pure Na. C. C. DAVIS

Electrolysis with a dropping mercury cathode. I. Deposition of alkali and alkaline earth metals. JAROSLAV HEYROVSKY. Univ. Prague. *Phil. Mag.* 45, 303-15(1923).—The deposition potentials of the alkali and alk. earth metals from soln. have been detd. by means of a dropping Hg cathode as follows: Li, -2.023 v.; K, -1.883 v.; Na, -1.860 v.; Cs, -1.837 v.; Rb, -1.796 v.;  $\text{NH}_4$ , -1.787 v.; Ca, -2.023 v.; Mg, -1.903 v.; Sr, -1.862 v.; Ba, -1.814 v. S. C. L.

The anode oxidation of gold. I. Anode oxidation of gold in sulfuric acid. FR. JIRSA AND OT. BURYÁNEK. *Chem. Listy* 16, 189-94(1922).—A detailed examn. is made of the oxidation of a gold anode in dil.  $\text{H}_2\text{SO}_4$ . The product is auric hydroxide, which loses a mol. of water on keeping over  $\text{P}_2\text{O}_5$ , giving the compd.  $\text{AuO}(\text{OH})$ , and this, on further dehydration, yields the oxide  $\text{Au}_2\text{O}_3$ .  $\text{O}_2$  is evolved during the passage of the current, and the amt. produced per amp. hr. for various concns. of acid is detd. The yields of hydroxide obtained with different currents and acid concns. are also measured. The solubilities of auric hydroxide, both freshly prepd. and stale, and prepd. both electrolytically and by hydrolysis, are detd. for different concns. of  $\text{H}_2\text{SO}_4$ , and from these results it is concluded that the product of soln. is auric sulfate, and not the compd.  $\text{Au}(\text{OH})\text{SO}_4$ . J. C. S.

Effects obtained with an alternating current sent through a capillary electrometer. R. D. KLEEMAN AND D. T. SIMONDS. *Phys. Rev.* 21, 38-45(1923).—In the capillary electrometer a. c. moves the thread of Hg in the same direction as d. c., *i. e.*, from the soln. to the Hg. This is in the opposite direction to the effect which should be pro-

duced by the d. c. component due to rectifying action. The magnitude of the effect varies linearly with the voltage up to 1.15 volts and then remains const. to 1.4 volts. Frequencies from 60 to 200 cycles give similar results. The *transition layer theory* furnishes a better explanation of the results than the Helmholtz double layer theory.

A. E. STEARN

On what does the adherence and size of electrolytic gas bubbles depend? A. CORN. *Z. Elektrochem.* 29, 1-5(1923).—Large gas bubbles which adhere to the electrode can only be obtained in acids at the cathode and in solns. of alkali at the anode. The size of the bubbles at first increases with the concn. of the electrolyte, then reaches a max. and finally falls off slightly. The bubbles are electrically charged with respect to the electrolyte: the bubbles formed at the anode in KOH are negatively charged, while those formed at the cathode in solns. of  $\text{H}_2\text{SO}_4$  are negatively charged in a dil. electrolyte and gradually become positively charged as the concn. increases. The adherence to the electrode of bubbles formed during electrolysis is due to electrostatic attraction between the charged bubbles and the electrode. H. JERMAIN CRIGHTON

Observations on sparking potentials. HILDEGARD STÜCKLEN. *Ann. Physik* 69, 597-624(1922). The effect of small amounts of water vapor upon the sparking potential in nitrogen. *Ibid* 625-7.—An app. is described with which it is possible by mech. scraping to give a new surface to electrodes in a vacuum sparking tube. Extensive expts. are described, dealing chiefly with the effects of adsorbed  $\text{H}_2\text{O}$  layers on the electrodes. This  $\text{H}_2\text{O}$  has no effect upon the sparking potential. It may be removed by scraping the electrode surfaces. Only in the case of Zn in  $\text{N}_2$  gas did any metal with a new surface show a different sparking potential from that with an old surface.

G. L. CLARK

Hall effect and specific resistance of evaporated films of silver, copper and iron. J. C. STEINBERG. *Phys. Rev.* 21, 22-9(1923).—The films were produced by moving a heated filament over the surface to be coated, at a distance less than the mean free path in a vacuum. They were hard, bright and resistant to corrosion. Though the grains were too small to be distinguished microscopically, X-ray analyses showed those of Ag and Fe and probably other metals, to have the same crystal structure as the bulk metals. For films 20 to  $200\mu$  thick the ratio of the sp. resistance of film to bulk metal for Ag, Cu and Fe are, resp., 15.2, 16.5 and 57.5. For the diamagnetic metals Ag and Cu the Hall coeff. of the films were, resp., 41% and 11% less than the bulk values while Fe showed an increase of over 500%. The max. intensity of magnetization in the Fe films was only half that attainable in bulk Fe, since the Hall effect is proportional to the magnetic field only up to 10,000 gauss instead of 20,000. For Ag and Cu the proportionality extends throughout the range of field intensity. The increase in sp. resistance is explained by the multiplication of contacts between grains. For Fe the limit of magnetization depends on the demagnetizing action of crystal poles which increases with decreasing size of crystal grains.

A. E. STEARN

Dielectric constants of some water solutions and their significance according to the dipole theory of Debye. (Also dielectric constants of some materials of biological and technological interest). REINHOLD FÜRTH. *Ann. Physik* 70, 63-80(1923).—Drude's second method (*Ann. Physik* 61, 486(1897)) was used to det. the dielec. consts. of water solns. of dextrose, levulose, raw sugar, carbamide, glyceroll, saccharin, gelatin and albumin. Three types of curves were obtained when the dielec. consts. were plotted against concns. In accordance with Debye's dipole theory (*C. A.* 6, 1087) the dielec. const. will decrease with increasing concn. of the soln. if the dipole moment of the solute is less than that of the solvent, such an effect appearing in the sugar solns. If the dipole moment of the solute is greater than that of the solvent the dielec. const. will increase with the concn. of the soln., at least in very dil. solns., but when measured



with an a. c. field, it may decrease at higher concn. because of the greatly increased viscosity. Such an effect was obtained with glyccoll, but carbamide gave a continually rising curve. Thus there should be an abnormal temp. effect on the dielec. consts. in solns. of high viscosity. A crystalloid may show a dielec. const. in soln. far different from what would be expected from that of the solid, because of the unordered condition in soln. "Mixture rules" for dielec. consts. may give results much in error. In electrolytes the ions are probably rather sym. in structure, whereas the undissociated mols. are strong dipoles, which explains the effects obtained in dil. and concd. electrolytes. The dielec. const. of dextrose and levulose (solid) is 2.2; of raw sugar, 4.9; carbamide, 3.5; saccharin, 9.5; gelatin, 5.6; albumin, 16.3; night blue, 4.4; Congo red, 20.0; methylene blue, 18.1; printer's black, 14.5; unsized paper, 3.4; sized paper, 4.2; starch, 11.6; dextrin, 8.0; casein, 8.0; hemoglobin, 14.2; cholesterol, 5.4; lecithin, 13.0; human, horse and guinea pig blood and serums, 85.0 to 85.5; human urine, 82.8; human milk, 75; cow's milk, 66; cream, 63; egg white, 68; egg yolk, 60; human saliva, 83.5; frog muscle, 83; brain gray matter, 85; brain white matter, 90; optic nerve (bovine), 89; and green leaf tissue, 83.

C. C. VAN VOORHIS

Composition of potassium chloroplatinate (VÜRTHEIM) 6. The occurrence of element number 72 (hafnium) in malacon and alvite (GOLDSCHMIDT, THOMASSEN) 8.

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### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

The increase of dispersion in the photoelectric spectra. RENÉ LEDRUS. *Compt. rend.* 176, 383-5(1923). W. F. MEGGERS

The calculation of the magnetic number of an atom in solution. J. H. SMITH. *Phil. Mag.* (6) 45, 375-8(1923).—A review and crit. discussion. S. C. L.

The field of an electron on Einstein's theory. S. J. GUNNINGHAM. *Phil. Mag.* (6) 45, 276-80(1923).—Mathematical soln. of the field equations for the case  $\lambda = \mu$  (cf. Hill and Jeffery, *Phil. Mag.* 41, 823(1921)). S. C. L.

A derivation of Planck's law of radiation by means of the adiabatic hypothesis. JAKOB KUNZ. *Phil. Mag.* (6) 45, 200-3(1923).—K. presents a simple and elegant derivation of Planck's radiation law  $dE/d\lambda = 8\pi hc/\lambda^4(e^{hc/\lambda K T} - 1)$  from the adiabatic hypothesis.  $E$  is the energy,  $\lambda$  the wave length,  $h$  Planck's const.,  $c$  the velocity of light,  $K$  a const., and  $T$  the temp. S. C. L.

The orientation of the Bohr-Sommerfeld orbits. A. W. CONWAY. *Phil. Mag.* 45, 324-6(1923). S. C. L.

Röntgen spectra and the periodic system of the elements. N. BOHR AND D. COSTER. *Z. Physik* 12, 342-75(1923).—A comprehensive summary of our knowledge of Röntgen spectra in their relation to the problem of at. structure, especially as regards the new Bohr spatial atom. Much of the exptl. material has been summarized by Coster (*C. A.* 16, 2636, 4132). The present paper gives a complete table of values of the X-ray energy levels, based on the latest exptl. data, in terms of  $T/R$  and  $\sqrt{T/R}$ , where  $T$  is the "term" in frequency units and  $R$  is the Rydberg const. The  $\sqrt{T/R}$  values are plotted against  $N$  (at. no.) to give the usual Moseley curves. These exhibit various discontinuities of slope, and these discontinuities furnish valuable evidence as to the process of formation of the various types of electronic orbits, especially in cases like that of the rare earths, where on the new Bohr theory an inner electronic group is being augmented. A sep. Moseley curve is plotted for each type of orbit, and each curve leads continuously into the visible region, where the orbit considered becomes a valence orbit and then a "virtual" orbit. This last stage is not studied. A theoretical study is made of the relative energy values to be expected for the various types of orbit and a good agreement with expt. is obtained. B. and C. make radically new assumptions as to the origin of the "screening" doublets and of the "relativity" doublets. On the familiar theory of Sommerfeld and Wentzel, the former type is due to two electrons of the same type, as regards radial and angular momentum, but differing in the "screening constant," this difference being indicated formally by a change in a third quantum number, not interpreted physically. The relativity doublets were considered due to two orbits of different shape, due to different amts. of angular momentum, but

having the same screening const. B. and C. assume, however, that the screening doublet orbits are of different shape and hence, by the new Bohr theory, of different screening consts., while the relativity doublets are due to orbits of the same shape but having different values for a new third quantum number  $k_2$ . B. and C. accept Sommerfeld's relativity formula, but thus essentially reject the theoretical derivation. The scope of the paper is indicated by the section headings: (1) Theoretical conceptions of at. structure. (2) Classification of Röntgen spectra. (3) Derivation of the energy levels from the exptl. material. (4) Theoretical estimates of the energy levels. (5) General comparison of the classification of the empirical Röntgen-levels with the theory of at. structure. (6) Theoretical meaning of the closer dependence of the energy levels on the at. no. (7) Concluding remarks.

R. T. BIRGE

**The relation of electron theory to atomic volume.** J. A. WASASTJERNA. *Finska Kemistsamfundets Medd.* 1920, 4 pp.—The concept of an atom as an elastic rigid sphere, which has led to satisfactory results in the theory of dielectrics of Clausius-Mosotti, and the equation of state of van der Waals, can be retained on the basis of the electron theory by considering the at. diameter to be that of the orbit of a rotating electron, and its vol. as defined by all possible orbits.

A. E. STEARN

**Separation of mercury into isotopes.** W. D. HARKINS AND S. L. MADORSKY. *J. Am. Chem. Soc.* 55, 591-601; *Nature* 111, 148(1923).—The sepn. was carried out in a large steel app. In each of a no. of runs 8 fractionations were made. The end cuts showed a difference of 0.1 of a unit in at. wt. A multiple-unit app. has been designed. Curves showing the relation between the increase in density of an isotopic mixt. and the cut are given.

L. D. ROBERTS

**Structure and energy content of atom nuclei.** TH. KALUZA. *Physik. Z.* 23, 474-6(1922).—From theoretical consideration of the energy relations resulting from the masses and elec. charges in atom nuclei built up of electrons and either H or He nuclei, K. concludes that the former kind can exist only under special stability conditions, but that the latter kind should show a positive charge such that  $A/zeZ = a \log Z + b$ , where  $Z$  is the charge on the nucleus and  $A$  the at. wt. This relation does not hold for the elements of at. no. less than 18 but is approx. true for those between 18 and 83, particularly for the ones with even at. nos. Above at. no. 83 the at. wts. are all larger than would be indicated by the theory.

C. C. VAN VOORHIS

**Electric figures on different materials, especially on crystals.** ELISABETH KARACHENKOVA. *Sitzb. Akad. Wiss. Wien. Abt. IIa*, 131, 156-69(1922); cf. Rubens, *C. A.* 15, 974.—Elec. figures produced by damped, high-frequency, high-voltage discharges on the surfaces of fragments of crystals were studied by dusting them either before or after the discharge. On an isotropic insulator a circle is produced, increasing in size with the voltage. When an anisotropic crystal, such as gypsum, is used, an elliptical figure is produced whose axes approach each other in length with higher voltages. At still higher voltages "creepage" brushes and sparks are produced. The negative sparks go in the direction of the longer axis, i. e., along the direction of smaller dielectricity. The radius of the figure varies inversely with the dielec. const. F. O. A.

**The range of  $\alpha$ -particles from polonium in various gases.** C. W. VAN DER MERWE. *Phil. Mag.* (6) 45, 379-81(1923).—The range of the  $\alpha$ -particles from Po in several gases was measured by means of the Wilson cloud method by photographing the tracks and selecting the longest one as the max. range. The stopping powers found are compared with those calc'd. by Bragg's law; the agreement is generally good. The following ranges in cm. at normal temp. and pressure conditions and stopping powers relative to air = 1 are reported: air, range 3.58 cms. stopping power 1.00; H<sub>2</sub> 16.28, 0.22, resp.; H<sub>2</sub>O vapor, . . . , 0.77; CH<sub>4</sub> 3.96, 0.91; N<sub>2</sub> 3.62, 0.99; CO 3.51, 1.02; O<sub>2</sub> 3.32, 1.08; NO<sub>2</sub> 3.23, 1.11; CO<sub>2</sub> 2.36, 1.52; SO<sub>2</sub> 1.97, 1.82; CH<sub>3</sub>Br 1.76, 2.04.

S. C. LIND

**The detonating action of  $\alpha$ -particles.** H. H. POOLB. *Sci. Proc. Roy. Dublin Society* 17, 93-5(1922).—Detonation of N iodide by the  $\alpha$ -particle has been shown by Henderson (*C. A.* 16, 4129), which suggests a probable explanation and the question as to whether there is a danger of  $\alpha$ -particles detonating common explosives. Two explanations are possible. The combined effect of two or more particles may be necessary. The  $\alpha$ -particle may strike a nucleus. Areas of iodide on filter paper were bombarded by particles from Ra C. The evidence favors the theory that a single particle causes the detonation. The detonating efficiency of an  $\alpha$ -particle at 1 cm. is about twice as great as that at 3 cm. Hg fulminate, Ag azide, dynamite, and nitroglycerin were not exploded.

L. D. ROBERTS

**Mechanism of  $\alpha$ ,  $\beta$  and  $\gamma$  ray emission.** E. MADGWICK. *Proc. Univ. Durham Phil. Soc.* 6, Pt. III, 136-47(1922).—The speed of  $\alpha$ -particles is a simple function of the no. of electrons in the at. nucleus. When the distance of the starting point of a particle from the center of the nucleus is calcd. from Geiger's measured velocities, assuming the inverse square law of repulsion, this distance is found to be a linear function of the no. of electrons in the nucleus. Since the size of the  $\alpha$ -particle can be taken as the size of its electrons, and since the law of inverse squares has been shown to hold to  $8 \times 10^{-13}$  cm., the values of this "starting distance," which reach  $6 \times 10^{-12}$  in some cases, indicate that the unstable portion of the nucleus has a "linear structure and is constituted chiefly of  $\alpha$ -particles." These are held together by forces of attraction. This is probable since the decrease in this distance per electron emitted is about  $3 \times 10^{-13}$  cm., and Chadwick and Bieler have shown (*C. A.* 16, 678) that for distances under about  $5 \times 10^{-13}$  cm. the law of inverse squares changes. The order of magnitude of these latter lengths is the same, so that if the first particle be displaced even slightly, the attraction is superseded by the ordinary repulsion and the particle is expelled. The nucleus as a whole is in rapid rotation and the movement of an  $\alpha$ -particle through one position outward involves an energy change of the same order of magnitude as that associated with hard  $\gamma$ -rays. This is a possible origin of  $\gamma$ -rays. The energy of a  $\gamma$ -pulse can be imparted to a  $\beta$ -particle and these latter probably derive their energies from hard  $\gamma$ -rays, the wide  $\beta$ -ray and  $\gamma$ -ray spectra being due to successive interchanges of energy, each one involving a sufficient expenditure of energy to liberate the electron from the atom.

A. E. STEARN

**The blackening law for  $\alpha$ - and  $\beta$ -rays.** W. BOTHER. *Z. Physik* 13, 106-12(1923); cf. *C. A.* 16, 4131.—This paper consists of remarks on a paper by Salbach (cf. *C. A.* 17, 361). B. considers that the Roscoe-Bunsen rule for blackening holds for  $\beta$ -rays, while Salbach thinks that it does not. The mode of expt. of Salbach is criticized because he used a weak source and did not take account of geometrical influences and absorption at other than normal emergence.

MARIE FARNSWORTH

**Radium: Its recovery, applications, and the present industrial situation.** HAROLD E. BISHOP. *Chem. Age* (N. Y.) 31, 52-4; *Science* 57, 341-5(1923).

E. H.

**The  $\gamma$ -rays of the radium and thorium families studied by their photoelectric effect.** M. DE BROGLIE AND J. CABRERA. *Compt. rend.* 176, 295-6(1923).—The method of analyzing the secondary  $\beta$ -ray spectrum, as used by Ellis (*C. A.* 16, 2071, 3805) and Meitner (*C. A.* 16, 2067, 2068, 3030), was modified so as to increase the sepn. of the lines. Ag, Ta, Pt, Au, Pb, and U were used as radiators of  $\beta$ -rays (from the stimulation of  $\gamma$ -rays from a tube of Ra).  $\beta$ -Rays from Ag, Sn, Ba, Au, and U, with the  $\alpha$ -rays from a tube of Meso-Th, also were studied. For Ra, the  $\beta$ -rays all come from the K level, while for Meso-Th with Au and U as radiators, they come from the L level. D. C. B.

**Radioactive decomposition products in the atmosphere and the probability of their origin in the sun.** II. HERMANN BONGARDS. *Physik. Z.* 24, 16-9(1923); cf. *C. A.* 14, 3357.—Further detns. were made of the activity of the atm. at altitudes high above

the earth's surface. Comparison of the activity through an interval of time with spectroheliographs of the sun taken at about the same times showed that the max. activity occurred when sun spots were facing the earth. The hypothesis of corpuscular radiations from the sun, part of which are intercepted by the earth, is discussed and evidence given for its support. D. C. BARDWELL

The effect of gases in facilitating the passage of current from an electron-emitting source in crossed electric and magnetic fields. O. W. RICHARDSON AND R. CHAUDHURI. *Phil. Mag.* (6) 45, 337-52(1923).—As is well known the passage of electrons through vacuum tubes is readily stopped by imposing weak magnetic fields in the direction perpendicular to the elec. intensity. But if a gas be admitted the flow of current to the anode through the magnetic field is greatly facilitated. Two possibilities are discussed: (1) the attachment of the electrons to gas mols. to form heavy negative ions which are much more difficultly arrested by the magnetic field; (2) the prevention, by mere collisions with, instead of attachment to the mols., of the free electrons from being stopped by the magnetic field. The theory of magnetic arrest is discussed; formulas are developed and a table is given showing the fields necessary to give the electrons different radii of curvature of path. Expts. were carried out with air, impure N, and chem. N. It is shown that in all cases the higher the gas pressure within limits of a few thousandths up to several hundredths mms. the greater the current owing to the ease with which electrons reach the anode. The difference between the residual current (after application of the magnetic field) in air and in pure N are not great, in spite of the much greater electron affinity of O. This appears to favor the second explanation, that of collision. It appears that a single collision of an electron with a mol. is sufficient to decide the fate of the electron in reaching or not reaching the anode. Some calcs. of mean free paths are made, based on rather wide assumptions. S. C. L.

The ionization by collision of hydrogen, nitrogen and argon. T. L. R. AVRES. *Phil. Mag.* (6) 45, 353-68(1923).—The principal object is to det. the ionization by collision in H, N and A for small ratios of voltage ( $X$  in v.) to gas pressure ( $p$  in mm. Hg) in the range  $X/p = 5$  to 60, where the actual pressures are varied from tenths of 1 mm. up to several mm. and in the case of A up to 60 mm. As in the earlier Townsend expts. the ultra-violet photocell. effect is employed to liberate the electrons. In H and N the values obtained for ionization by mol. collision both of the electrons ( $\alpha$ ) and of the positive ions ( $\beta$ ) are in good agreement with the earlier values (*Phil. Mag.* 3, 557(1902); 6, 598(1903)). The ionizing effect of the electrons was observed as low as  $X/p = 5$  in H, and  $= 10$  in N; the effect of the positive ions was observed as low as  $X/p = 30$  in H,  $= 100$  in N. Slight contamination of the gases appears to have but little effect. The nature of the electrodes (Ag, Zn and brass) appears to have no influence on the process by which the current is increased with the distance between the electrodes. In A the values of  $\alpha/p$  and of  $\beta/p$  corresponding to the lower values of  $X/p$  were larger than those previously obtained; otherwise the agreements were good. The effects of electrons in A were observed as low as  $X/p = 2$ , and of positive ions at  $X/p = 10$ , but in contaminated A not below 20. The effect of impurities was greater in A than in H and N, and was found to increase the sparking potentials in all cases.

S. C. LIND

Magnetization, rotation and atomic structure. S. J. BARNETT. *Physik. Z.* 24, 14(1923).—A criticism and correction. Cf. W. Braunbek (*C. A.* 16, 4126). C. R. P.

The influence of the gas content on the thermal and photoelectric emission of platinum and tantalum. RUDOLF SHURMANN. *Z. Physik* 13, 17-34(1923); cf. *C. A.* 16, 2257.—By using the app. as previously described, it is found that the electron emission is retarded by careful gas removal. The change in the size of the space charge is related directly to the temp. of heating and the amt. of gas removal. The change is greater,

the lower the temp. of heating and the more strongly the metal is freed from gas. This effect is explained through the assumption of a cloud of negative gaseous ions which are given out by the metal foil and which carry the charge. This ion cloud is larger with more gas in the foil and with a higher temp. The const.  $A$  in the Richardson equation for the change of current with the temp. decreases by about  $10^3$  for strong gas removal. Thus the decrease in the no. of free electrons in the metal also brings about a lowering of the emission with gas removal. The const.  $b$  and therefore the work of emergence,  $\phi$ , remains constant for Ta and changes only a little for Pt. M. F.

**Electrons from hot filaments.** ANON. *Elec. World* 81, 384(1923).—Dushman's equation for the relation between electron current and cathode temp. is more simple than that of Richardson, as it requires only one const. for each different cathode material. A thoriated W cathode gives a current at  $1500^\circ\text{K}$ ., which is 130,000 times greater than from pure W. Some other added metals cause an even greater value. The addn. of small amts. of the proper gas to the tube reduces the voltage necessary to overcome space charge. With very high voltages some current will flow at room temp. The Th on the surface of a W filament is only about 1 atom, or one one-hundred-millionth of an inch thick. Water vapor is very injurious to this film, and is removed by metallic Mg. Too high a temp. (above  $1700^\circ$ ), will evap. the film. In most applications the electron currents are controlled by the voltage change on the grid modifying the space charge. It may also be controlled by a magnetic field from an external coil or by several other methods. W. E. RUDER

**Ionization produced by the hydration of quinine sulfate.** MILLÉ CHAMÉ. *Compt. rend.* 176, 251-3(1923).—C. measured the increase in wt. of quinine sulfate during its hydration by means of a Curie balance. The rate of change of ionization during hydration was also noted. There is indicated a distinct relation between the two phenomena. From the results obtained a mathematical expression is derived for  $Q$ , the total quantity of electricity discharged during hydration of the salt. L. T. FAIRHALL

**The opacity of an ionized gas.** J. Q. STEWART. *Nature* 111, 186-7(1923).—Radiation is selectively scattered by bound electrons: it is non-selectively scattered and absorbed by free electrons. An ionized gas contains free electrons and therefore should be opaque. The vapor of an iron wire exploded by a high voltage is opaque. At a depth in the sun's atm. corresponding to a pressure 0.01 atm. the ionized gas is sufficiently opaque to cut off all radiations from a greater depth. F. E. BROWN

**Location of energy.** H. BATEMEN. *Science* 57, 238-40(1923).—The mass of an electron has been calcd. on the basis of the modification of electromagnetic theory recently proposed (cf. *Phys. Rev.* 20, 243). This calcn. has led to the surprising result that the mass inside an electron in uniform motion, when calcd. from the momentum, is equal but opposite in sign to the mass outside. It may be advantageous to regard the mass of an electron as being situated inside the electron rather than outside. The probability of this point of view is discussed. H. JERMAIN CREIGHTON

**The effect of an electric field on the viscosity of a gas.** H. SIKK. *Z. Physik* 13, 35-47(1923).—A calcn. is made of the correction to the viscosity of a gas when an elec. field is applied normally to a layer of mols. moving with uniform velocity. This correction is required because of the elec. character of the atoms composing the mols. The effect of the elec. field is to reduce the viscosity coeff. Results calcd. for O and N are confirmed by the exptl. results of Ray (*C. A.* 16, 2636). F. O. A.

**Magnetic valency and the radiation hypothesis.** F. T. PIERCE. *Phil. Mag.* (6) 45, 317-23(1923).—A qual. treatment of the radiation hypothesis of chem. action from the standpoint of a magnetic theory of valence bonds involving the quantum hypothesis. The phys. picture presented appears to be of sufficient promise to warrant the testing of its ability to explain spectroscopic phenomena. S. C. L.

Luminescence of compounds formed by the action of magnesium on *p*-dibromobenzene and related compounds. W. V. EVANS AND R. T. DUFFORD. *J. Am. Chem. Soc.* **45**, 278-86(1923).—*p*-Bromophenylmagnesium bromide (*A*), is prep'd. and its properties in soln. are studied. Its luminescence is compared with that of other aromatic halogen compds., when exposed to the action of air and  $O_2$ . Other gases,  $CO_2$ ,  $H_2O$ ,  $SO_2$  and  $N_2$ , produce no luminescence. The spectrum of the chemiluminescence of *A* is investigated by the use of light filters; its lower and upper limits lie within the region  $\lambda 5200$ – $\lambda 3500$ , and are distinct from associated fluorescence spectra. Photographs of two kinds of fluorescence are obtained from the oxidation products, one giving a single-banded spectrum, the other a quite different multibanded spectrum.

E. P. WIGHTMAN

Series and other regularities in the spectrum of manganese. M. A. CATALÁN. *Phil. Trans. Roy. Soc. London* **223A**, 127-73(1922).—Kayser and Runge's work of arranging in series the triplets of the arc spectrum of Mn is extended to new lines, resulting in a principal series  $1s - mp$  of 4 members; a sharp series  $1p - ms$  of 5 members; a diffuse series  $1p - md$  of 4 members; and a fundamental series  $2d - mf$  of 2 members. The characteristic triplet septs. are  $\Delta\nu_1 = 173.7$  and  $\Delta\nu_2 = 129.2$ . Of particular interest is the structure of the first member of the diffuse series, which consists of 9 lines instead of 6, as for the alk. earths; that is, each line of the triplet is itself a narrow triplet. There exists also in the spectrum a pair of lines sepd. by the frequency difference  $\Delta\nu_2 = 129.2$ . These are the intercombination lines  $1S - 1p_2$  and  $1S - 1p_1$ . From them a value of  $1S$  is found which leads to the establishing of the series systems corresponding to the singlet systems of the alk. earths. In Mn, however, the series  $1S - mP$ ,  $1P - mS$ , and  $1P - mD$  are composed of narrow triplets instead of single lines, the triplet septs. being  $\Delta\nu_1 = 44.1$  and  $\Delta\nu_2 = 35.8$ . Parallel to this series system is a second system of series of narrow triplets with septs.  $\Delta\nu_1 = 14.2$  and  $\Delta\nu_2 = 8.7$ . The members of the parallel series are found by adding a const.  $C = 10967.75$  to the wave nos. of the corresponding members of the series  $1S - mP$ , etc. Since  $1S$  is known, it is possible to calc. from the quantum theory the resonance and the ionization potentials of Mn, which are 2.29 v. and 7.41 v., resp. In addn. to the series triplets there are groups of 9, 13 and 15 lines, characterized in part by the triplet frequency differences just given and also by new frequency differences which are the same for all the groups. To such groups the name multiplet has been given. In all, 10 multiplets have been worked out which belong to the arc spectrum of Mn. In the spark spectrum of Mn, which is emitted by the ionized atom, there also occur triplets and multiplets. Of the triplets one is apparently the first member of a principal series and the other belongs to the diffuse series, because it is composed of 9 lines, resembling in this respect the wide diffuse triplet of the arc spectrum. Preliminary examn. of the spectra of other elements shows the existence of multiplets for Cr, Mg, Ca, Sr, Ba, Si,  $Al^+$ ,  $Sc^+$ ,  $Y^+$ , and  $La^+$ . Theory indicates that if the no. of outer electrons of an atom is odd the spectrum will consist of doublets, and if even, the spectrum will consist of triplets. On this basis neutral Mn might be expected to emit a doublet spectrum and  $Mn^+$  a triplet spectrum. But there is reason to believe that in both the neutral and ionized states the Mn atom has 2 electrons in the outermost ring, the loss of one by ionization being accompanied by a transition of an electron from an inner ring to the outermost. This would account for the fact that triplet series are characteristic of both the arc and spark spectra of Mn. A table of wave lengths is given in which all lines that belong to series triplets or multiplets are classified.

C. C. KIESS

The structure of the arc spectra of the elements of columns VI and VII of the periodic table (I). M. A. CATALÁN. *Compt. rend.* **176**, 84-5(1923).—C. has already shown that the diffuse triplets of Mn are composed of 9 lines arranged in groups of 3

(cf. preceding abstr.). A similar structure holds for Cr. Moreover, the arc spectrum of Cr exhibits several systems of series, 2 of which, constituting parallel systems, are tabulated. In addn. to the series the spectrum also contains groups of lines which form multiplets. C. C. KRESS

**Remarks on the structure of the spectrum of chromium.** A. DE GRAMONT. *Compt. rend.* 176, 216-7(1923).—From the analogy of sensitive triplets in the spectra of Cr and Mn two sets of triplets in Cr were suggested (C. A. 17, 492) as related to principal series. The series regularities for Cr have since been outlined by Catalán (preceding abstract) and it is emphasized that knowledge of the most sensitive lines of spectra has value for the discovery of series, still unknown for most of the chem. elements.

W. F. MEGGERS

**Band spectra of mercury.** H. NAGAOKA. *Japan. J. Physics* 1, 1-6(1922).—The discordant results found in the study of the band spectra of Hg are attributed to differences in the construction of the lamps, to avoid which a new form of lamp was designed. It consisted of a water-jacketed vessel hollowed out of solid iron. The vessel was closed by means of a thick iron lid, at the center of which was placed a right-angled quartz prism. A cylinder to which was attached a tube of silica glass was screwed to the bottom of the iron vessel. An invar electrode at the bottom of the tube formed the anode. Hg was poured into the vessel and the tube until it reached the upper end of the silica tube. The arc was established between the Hg inside the silica tube and the Hg outside of it. The lamp, which used a current of from 3 to 6 amps., was exhausted by means of a Gaede Hg pump and a condensation pump in series. To obtain well defined spectra the pumps were kept going continuously. The spectrum was photographed by means of a Fuess quartz spectrograph, in order to det. the heads of the bands. The dispersion of the quartz prism was not sufficient to det. these heads accurately. A concave grating of high resolving power must be used for this purpose. The structure of the bands was studied by means of a quartz Lummer-Gehrcke plate. The photograph of the interference points thus obtained shows in each of the lines a distinct gradation as the order of the spectra gradually decreases. Apparently each line has no companion in the form of satellites. Later expts. with a Hilger spectrometer and Fabry-Perot interferometer were made. The interference points thus obtained gave no distinct evidence for the complexity of the band lines. In two lines the interference points suggest that higher dispersion might resolve the lines into principal and attendant satellites. A. W. SMITH

**Simple method for the measurement of ultra-violet absorption.** CHR. WINTHER, BAGGESGAARD-RASMUSSEN AND F. SCHREINER. *Z. wiss. Phot.* 22, 33-46(1923).—Merton's method for quant. photographic measurement of absorption (C. A. 7, 1447) was adopted for use in the ultra-violet. Measurements were made on  $\text{KNO}_3$  and  $\text{AgNO}_3$  and also with an *improved fluorometer*. The results were confirmed by thermo-elec. measurements. G. R. FONDA

**Notes on standard wave lengths, spectrographs, and spectrum tubes.** W. F. MEGGERS AND KEVIN BURNS. *Bur. Standards, Sci. Papers* No. 441, 185-99(1922).—Standard wave lengths in the *cadmium spectrum* are presented in the range 2980 to 5085 Å. The values for 13 lines are given relative to the primary standard and are thought to be correct to one part in several millions. A quartz rock-salt spectrograph, designed for the purpose of photographing interference phenomena in the ultra-violet, is described. The characteristics and performance of a *stigmatic concave grating mounting* are outlined, and detailed drawings of the app. are reproduced. Instructions and suggestions are given for the prepn. of spectrum tubes commonly required for optical demonstration, testing, or research. E. H.

Light absorption in a pleochroitic uniaxial crystal (a green tourmaline from Minas



**Geraes in Brazil.** J. A. WASASTJERNÅ. *Oversikt Finska Vetenskaps-Soc. Forh.* **64**, No. 1, 1-8(1922).—An exptl. detn. of the dependence of light absorption on the wave length and oscillatory direction of light in a pleochroitic uniaxial crystal. The coeff. of absorption  $\alpha$  as a function of  $g$ , the angle which the plate of tourmaline forms with the axis of the crystal (the oscillatory direction of the extraordinary ray) is indicated by the equation  $\alpha/N^2 = A^2 \cos^2 g + B^2 \sin^2 g$ , where  $N$  is the index of refraction and  $A$  and  $B$  are constns.

HARRY B. WEISER

**Wave-length measurements in the arc spectra of neodymium and samarium.** C. C. KRISS. *Bur. Standards, Sci. Papers* **18**, 201-19(1922).—The arc spectra of Ne and Sa were photographed with a large concave grating spectrograph, the photographic plates being suitably sensitized to record the spectra from the green to the infra-red. About 1500 lines were measured in each spectrum, most of them being of low intensity. No bands were observed in either spectrum, although a few unsym. lines may be regarded as band heads. About 125 lines common to both spectra have been segregated into a sep. table. These lines may be characteristic of the element of at. no. 61, which comes between Ne and Sa but which has not yet been isolated. The materials used for the work were Ne oxalate and Sa oxide prepd. at the Univ. of Ill. and Sa oxalate prepd. at New Hamp. College. This work is a continuation of a study of the spectra of the rare earth elements of which a first report is given in *C. A.* **16**, 383. C. C. K.

**Spectral analysis investigations to disclose a heretofore unknown element of the terbium group, and the arc spectrum of terbium.** J. M. EDER. *Sitzb. Akad. Wiss. Wien Abt. IIa*, **131**, 199-298(1922).—Fractionations of the rare earths Tb, Dy, and Gd by Urbain and by Welsbach led to comparatively pure Tb. In 1920 E. gave the history and bibliography of these investigations (*C. A.* **15**, 3422) and mentioned his spectrographic work on Welsbach preps. of various Tb, Dy and Gd fractions which have led to indications of one or more unknown elements. Reduction of spectrograms of various fractions has made it possible to define the arc spectrum of Tb. A table of several thousand lines from 2400 to 7257 Å. is given in international units. No evidence for a new element between Gd and Tb is found, but many lines which are absent or weak in the purer elements are found in intermediate Tb-Dy fractions. These are included in the table and are presented as evidence for the existence of a new element, for which the name "Welsium" is proposed in honor of the eminent discoverer of rare earths, Carl Auer v. Welsbach.

W. F. MEGGERS

**The combination principle and some new types of bands.** ERIK HULTHÉN. *Z. Physik* **11**, 284-93(1922); cf. *C. A.* **16**, 202.—The validity of the combination principle for band spectra is extended from mols. at rest to those in rotation. The structures of two types of bands ascribed to Zn, Cd and Hg are investigated and it appears probable that the source of the bands in each case is a dipole of the element and N.

W. F. MEGGERS

**The combination principle and a new class of bands.** A. KRATZER. *Z. Physik* **13**, 82-4(1923).—K. remarks that the work of Hulthén (cf. preceding abstr.) can be improved upon by changing the numbering of the lines and thus include all the bands into a single class. The general formula is given but its theoretical derivation will be given later.

W. F. MEGGERS

**Theory of anomalous Zeeman and magnetomechanical effects.** A. LANDÉ. *Z. Physik* **11**, 353-63(1922).—A mathematical discussion of electronic motions in a magnetic field. Additional precession and rotation derived from empirical Zeeman types by the analogy principle leads to half-quantum units for the valence electron and for the trunk of doublet-line atoms and explains the anomaly of the Barnett and Einstein-de Haas effect. Cf. *C. A.* **16**, 1183, 1184.

W. F. MEGGERS

**Regularities in the red spectrum of xenon.** L. A. SOMMER. *Z. Physik* **13**, 85-93

(1923).—The existing wave-length data on 148 lines and corresponding vacuum wave-numbers are tabulated. 142 lines are arranged in 25 groups of nearly const. wave-number differences ranging from 58 to 5840. The ultimate object is to compare the spectrum of ionized Cs with this red spectrum of Xe. W. F. MEGGERS

**The intensity of complex lines.** H. B. DORGELO. *Z. Physik* 13, 206–10(1923).—A method is described for detg. relative intensities of the doublets in different spectral series of the alkalis. It is based on the principle that two light intensities of the same (or nearly the same) wave length are equal, if they produce, with equal exposures on the same photographic plate, the same blackening. The arc spectra of the alkali metals were photographed through a series of calibrated screens imaged on the slit of a spectrograph, and the spectrograms were then measured with a microphotometer. The lines with greater wave lengths in the sharp and diffuse doublet series of Na, K and Cs appear to be about twice as intense as the shorter wave-length companions.

W. F. MEGGERS

**Arc spectra of metals in various media and in vacuo.** St. PROCOPIU. *Compt. rend.* 176, 385–8(1923).—Modifications in arc spectra of Cu, Au, Zn, Cd, Mg, Ca, Al, and C are observed when the arc is operated in different surroundings. The spectral region studied was between 5000 and 2100 Å. The arc spectra of all these metals showed broadened lines and weakening or vanishing of higher members in series when the arcs were in water, H or illuminating gas. In N<sub>2</sub> the arc is stable; it shows more lines than air and many of the lines are reversed. In vacuo, the arc spectra show more extended series and numerous reversals especially at the cathode; flame lines are weak but spark lines appear strongly and often reversed.

W. F. MEGGERS

**The spectrum of neutral helium.** W. M. HICKS. *Nature* 111, 146(1923); cf. C. A. 17, 365.—Silberstein's expression for the diffuse series He D'(C. A. 17, 1188) shows deviations hundreds of times greater than observation errors. The possibility of representing this series roughly in the form  $A - N/m^2$  is explained. W. F. MEGGERS

**The computation of non-hydrogenic spectra from motions of electrons about central forces.** I and II. E. FUGS. *Z. Physik* 11, 364–78; 12, 1–12(1922).—In 1916 Sommerfeld gave a theoretical derivation for the Balmer, Rydberg and Ritz spectral series formulas as 1st, 2nd and 3rd approximations of the energy of an electron moving in a central field. It was impossible, however, to compute the empirical series consts. Part I derives the general type of potential function from the empirical spectra and shows why the series consts. could not be computed. Part II discloses a way of detg. the potential gradient inside the atom from the spectral terms, the spectrum of Na being taken as an example. The original papers must be referred to for quantum theory and mathematical details.

W. F. MEGGERS

**Report on the fine structure of near infra-red absorption bands.** H. M. RANDALL. *J. Optical Soc. Am.* 7, 45–57(1923).—A review of recent exptl. and theoretical work on the structure of the absorption bands of certain gases (HCl, HBr, HF, CO<sub>2</sub>, CH<sub>4</sub>, and water vapor) which lie in the near infra-red region of the spectrum. W. F. MEGGERS

**The structure of arc spectra of molybdenum, selenium and chlorine.** M. A. CATALLAN. *Compt. rend.* 176, 247–8(1923).—Wave lengths and numbers are given for one system of series, principal, sharp and diffuse, for Mo. The diffuse term is quintuple and gives 9 components for each line of this series. New measurements in the Se spectrum will probably show a quintuple diffuse term as in Cr and Mo. The spark spectrum of Cl shows triplets and although the tables give only 1 + 3 + 2 components the first line will probably be found to be triple and thus resemble the triplets in Mn.

W. F. MEGGERS

**Ultra-violet absorption spectra of aniline and of some toluidines.** F. W. KLINGSTEDT. *Compt. rend.* 176, 248–50(1923).—The ultra-violet absorption spectrum of a

soln. in hexane of aniline exhibits a group of 9 narrow bands between  $\lambda 2991$  and  $\lambda 2704$  followed by a broad band at  $\lambda 2340$ . Const. frequency differences exist between the narrow bands. When  $H_2O$ , alc. or  $CCl_4$  is used as a solvent, the narrow bands fuse into a single broad band, a behavior similar to that of phenol and the diphenols. The absorption spectrum of *o*-toluidine is characterized by two broad bands while that of *p*-toluidine presents 7 narrow bands followed by a broad band in the extreme ultra-violet. Wave-length tables and curves exhibit the quant. results of the investigation.

C. C. KIRSS

**Tesla spectra and the Fraunhofer effect in complex compounds.** J. K. MARSH AND A. W. STEWART. *Nature* 111, 115-6(1923).—Benzene vapor at low pressure when excited by waves from a Tesla transformer emits a luminescence spectrum composed of band groups, all of which have the same structure. A group consists of 4 strong bands each accompanied by a weaker band and then 2 broader and weaker bands. The band groups are comprised between the wave-number limits  $\nu = 3149$  and  $\nu = 3752$ . The wave numbers of the bands are given by  $\nu = 98.712 n - (98.712 m/6)$ , where  $n = 33, 34, 35, \dots$ , and  $m = 0, 1, 2, \dots$ . The full fluorescence spectrum of benzene coincides with part of the luminescence spectrum if it is shifted by a small const. amt. Furthermore the bands of the absorption spectrum agree very closely with the emission bands just described, thus establishing for the first time the Fraunhofer effect in the case of the spectrum of an org. compd. of complex structure.

C. C. KIRSS

**The disappearing gap in the spectrum.** O. W. RICHARDSON. *Nature* 111, 118-21, 153-5(1923).—A popular lecture reviewing recent progress, made since 1913, in exploring the spectral region between  $900\text{\AA.}$ , the shortest ultra-violet ray observed at that time by Lyman with the vacuum grating spectrograph, and  $8\text{\AA.}$ , the longest X-ray wave observed by Moseley with the crystal spectrometer.

C. C. KIRSS

**An extension of the fundamental infra-red absorption band of hydrogen chloride.** W. F. COLBY, C. F. MEYER AND D. W. BRONK. *Astrophys. J.* 57, 7-19(1923).—By the aid of a grating particularly bright in the region in question, the HCl fundamental absorption band at  $3.4\mu$  was extended from  $3.9$  to  $4.2\mu$ , 7 new principal lines being found. The present total, 39, gives an accurate empirical formula and permits improvement of Kratzer's theoretical formula. To obtain the longest lines it was necessary to raise the temp. of the gas to about  $500^\circ$ , and under this condition a new group of faint lines is found between  $3.8$  and  $4.1\mu$ , with spacing different from that of the fundamental group. These may correspond with a change of radial quantum from 1 to 2, but the frequencies do not agree with the predictions of Kratzer.

K. BURNS

**The production of colored flames for use with spectrometers and polarimeters.** J. J. MANLEY. *Phil. Mag.* 45, 336-7(1923).—An extremely simple and serviceable device is described to effect the usually troublesome operation of feeding salt solns. to maintain colored flames. Near one end of a tube 20 cm. long and 1 cm. in diam. a bulb is blown contg. about 20 to 30 cc. The short end is bent at a right angle and fitted with a vitreous tube 8 cm. long and 5 mm. diam. with a bore of 1 mm., projecting slightly into the glass tube against a slight constriction. A wick is made by putting through the horizontal vitreous tube a few fine Pt wires which carry the soln. contg. the desired salt from the reservoir to the flame. Any desired head may be obtained by changing the tilt. Operation is continuous, requires no attention, and a no. of different containers may be kept constantly ready with different salts without the necessity of cleaning up the feeding device upon changing from one to another.

S. C. LIND

**The visibility of individual spectra.** F. H. NEWMAN. *Phil. Mag.* 45, 293-9 (1923).—Following a discussion of the production of spectral lines with reference to electronic energy, some expts. with alkali amalgams in a silica discharge tube are reported. The temp. was kept const. to maintain const. partial pressures of the vapors.

When the induction coil used for excitation was operated with an ordinary make-and-break, the alkali metal lines predominated. With a Wehnelt interrupter the Hg lines appeared. With a condenser discharge the Hg spectrum became very bright. The difference is attributed to the increased energy in the last case, enabling the metal with the higher ionization potential (Hg) to become ionized. S. C. LIND

**The destruction by light of the fluorescent property in fluorescing solutions and the photochemical equivalent law.** P. PRINGSHEIM. *Z. Physik* 10, 176-84(1922).—Perrin's expts. (*C. A.* 13, 3078) on the destruction of the fluorescence of certain org. substances by ultra-violet light have been repeated and the results confirmed. The destructive effect depends on the light concn. At low temps. the intensity of fluorescence is not changed appreciably, the chem. reaction being almost entirely prevented. Perrin's theory that fluorescence is an accompaniment of chem. transformation is untenable. On the other hand either fluorescence or chem. transformation is of consequence for the validity of the photochem. equiv. law. (See following abstract.)

HARRY B. WEISER

**The fluorescence of esculin.** J. C. McLENNAN AND F. M. CALE. *Proc. Roy. Soc.* 102A, 256-68(1923).—The fluorescent power of solns. of esculin in  $H_2O$  can be destroyed by an acid but it is restored by the subsequent addition of alkali. If solns. are subjected to ultra-violet light or ozonized  $O_3$  the fluorescent power is destroyed completely. The action of  $O_3$  causes a faint chemiluminescence. Solns. sealed in glass tubes fluoresced strongly for hrs. when treated with violet or ultra-violet light of the longer wave lengths, without exhibiting any loss of fluorescent power; solns. sealed in quartz tubes gradually lost this power. The results show that the emission of fluorescent light by an org. substance is not generally accompanied by its destruction as held by Perrin (*C. A.* 13, 3078).

HARRY B. WEISER

**Phosphorescence and phototropy of some metallic sulfides.** J. R. MOURELO. *Mon. sci.* 12, 177-88, 249-60(1922).—An historical survey of the phenomena of phosphorescence and phototropy together with an account of observations on a no. of luminescent sulfides. The importance of both the diluent and the impurity, the phosphorogene, is emphasized and the theories to account for the luminescence are discussed. The electronic theory assumes that a bombardment of electrons sets up a reaction in the diluent which serves to accelerate a luminescent reaction of the phosphorogene. The mixt. possessing the max. sensibility to light may show the phenomenon of phototropy. It is argued that this theory, which is the most attractive, explains the mechanism but not the cause of the phenomena. The numerous tentative hypotheses that have been proposed are valuable but a completely satisfactory theory has not been formulated.

HARRY B. WEISER

**The mechanism of photochemical processes. II. The behavior of dry hydrogen and oxygen.** ALFRED COEHN AND HEINRICH TRAMM. *Ber.* 56B, 455-8(1923).—Mixts. of  $2H$  and  $O$  which had been dried with the greatest care reacted only very slowly and with a little flame at red heat, at which a moist mixt. exploded violently. Under exposure in quartz tubes to ultra-violet light from a quartz Hg lamp 20% of the gases had reacted after 5 hrs. whether moisture were present or not. In both respects  $H$  and  $O$  behave similarly to  $CO$  and  $O$  (cf. *C. A.* 16, 205). III. **The action of drying on the union of chlorine and hydrogen.** *Ibid* 458-62.—A mixt. of  $Cl$  and  $H$  dried with the greatest care was exposed in quartz tubes to a 100 c. p. Osram lamp. No  $HCl$  whatever was formed, although a mixt. with a 10-mm. moisture pressure reacted completely in 12 min. On the assumption that the dissociation of the  $Cl$  is necessary for the reaction, this is in agreement with results showing that dissociation requires a greater no. of quanta than were present in the authors' reaction expts. and suggesting that the  $H_2O$  serves to form  $Cl$  atoms by a secondary reaction requiring less

energy. Similar expts. with Cl and CO showed that the speed of the reaction to form  $\text{COCl}_2$  was retarded in the complete absence of moisture. The decompn. of completely dried HBr and HI under the same conditions proceeded at the same rate as in the presence of moisture, but with HCl its decompn. took place only in the presence of moisture.

G. R. FONDA

Various photoelectrical investigations. W. W. COBLENTZ. *Bur. Standards, Sci. Papers* No. 462, 586-607(1922).—Miscellaneous data are given on the photoelec. sensitivity of various natural and artificial substances, and the effect of heat and elec. treatment. The prepn. and testing of various Mo sulfides are described. Photoelec. sensitivity is inherent in  $\text{MoS}_2$  alone, artificial prepn. whether by wet or dry process having far less sensitivity than sensitive spots of the natural mineral. Sensitive natural mineral appears to have a higher Fe content than the non-sensitive material. Slow heat treatment of molybdenite has no permanent effect upon the sensitiveness up to  $500^\circ$ ; at  $600^\circ$  it is permanently decreased and is destroyed at  $700^\circ$ . The heat treatment of stibnite has no effect, even on fusing, except a possible shift of the max. sensitiveness to the longer wave lengths. An a. c. had no effect upon stibnite and molybdenite other than that due to the heat effect with large currents. Artificial prepn. of the following showed no marked sensitiveness, Mo oxide, various Sn, W, and U sulfides, also  $\text{Bi}_2\text{Te}_3$ ,  $\text{MoSe}_2$ ,  $\text{AgNO}_3$ , and  $\text{KNO}_3$ . Data are given confirming the negative spectrophotoelec. reaction of molybdenite. A sample of molybdenite was found with a uniform sensitiveness over a wide range of the visible spectrum, and a photoelec. reaction proportional to the intensity of the radiation stimulus. In the extreme ultra-violet molybdenite and stibnite have no sharp bands of photoelec. sensitiveness but reaction gradually decreases with decrease in wave length. Several spectral response curves are given of Case's Ba and Sr photoelec. cells, which have maxima at  $0.42\mu$  and  $0.39\mu$ , resp. By covering the Ba cell with a suitable screen, a spectral response curve is obtained which coincides closely with the visual response of the av. eye. Data are given on the spectro-photoelec. reaction of  $\text{Cu}_2\text{O}$ , also of  $\text{Pb}_2\text{SbS}_3$ , which show that its spectrum for a compd. is not the composite of the reactions of the constituents which may be photoelec. active. Iodine was found to be sensitive with a max. in the region  $0.53\text{--}0.55\mu$ .

S. L. CHISHOLM

The absorption spectra of tanning extracts (BRUÈRE) 29. Colloid chemistry and photochemistry (SCHAUM) 2. The occurrence of element number 72 (hafnium) in malacon and alvite (GOLDSCHMIDT, THOMASSEN) 8. Crystal structure of natural and of synthetic oxides of uranium, thorium and cerium (GOLDSCHMIDT, THOMASSEN) 8. Selenium cell or bridge (U. S. pat. 1,447,646) 1.

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## 4—ELECTROCHEMISTRY

COLIN G. FINK

**Water powers of Norway.** C. N. ANDERSON. *Elec. World* 24, 677-82(1923).—Brief descriptions of the most important power plants, including costs for power, utilization, etc. Of the total hydroelectric power generated to-day, 60% is used in electrochem. industries such as cyanamide, nitrates, carbide, zinc, etc., and about 20% in the pulp and paper industries. C. G. F.

**Gray-iron castings from electric furnace.** I. J. BARTON. *Iron Age* 111, 269-73 (1923).—A comparison of acid and basic practice. Gray Fe was made on an acid bottom by melting cast Fe borings, gray-Fe scrap or steel scrap. Hard Fe and hard spots in the product were frequent; the Fe was always dirty; trouble was encountered from heavy slags caused by the reduction of  $\text{SiO}_2$  from the hearth; control of C and Si in the metal was impossible. After changing to a basic-lined furnace it was much easier to obtain soft Fe; dirt and inclusions were eliminated; there was no reduction of the hearth, thus making it easier to obtain high C and to control Si; defective castings were almost entirely eliminated. LOUIS JORDAN

**The use of electricity in steel works.** WM. M'FARLANE. *J. West Scotland Iron Steel Inst.* 30, 34-49(1923).—Comparisons are made to det. the advisability of steel works purchasing elec. power, as against generation at the plant. Public supply tariff depends upon (a) the running charge, (b) the max. demand charge. The first factor is generally proportional to fuel costs. Keeping the factor (b) low considerably reduces the investment costs. From an analysis based on this interpretation the author concludes that a plant with high load factor can purchase electricity economically. Where the load factor drops to 40%, as in steel works, local generation is better. A. H. D.

**Electric brass furnace practice.** H. W. GILLETT AND E. L. MACK. *Bur. Mines, Bull.* 202, 319 pp.(1922); cf. C. A. 14, 1784, 2133, 2753, 3195.—A report too comprehensive to permit abstracting. Numerous tables, illustrations, and both subject and name indexes are included. The purpose of the report is to present available information on what com. elec. brass furnaces are doing and can do, and to show, by description and exptl. test data, the evolution of present furnace types, including information on failures as well as on successes. Fundamental principles of design, construction, and operation are also considered. After a discussion of theoretical and practical advantages of elec. brass melting, of the distinction between steel-melting and brass-melting elec. furnaces, and the classification of elec. brass furnaces, the individual furnaces are considered under the following classes: (a) crucible furnaces, either lift-out or tilting; (b) hearth furnaces heated by a resistor, a smothered arc, a direct arc, or an indirect arc, the last two types in both stationary and moving furnaces, or by induction in a horizontal ring, a vertical ring, or a high frequency furnace. In conclusion are considered the factors governing the choice of a particular furnace, the relation of the central station, the cost of power, methods of testing furnaces, and the conservation possible in metals, crucibles, labor and health, and fuels. LOUIS JORDAN

**Desulfurization of pyrite cinders in the electric furnace.** G. ONGARO. *Giorn. chim. ind. applicata* 3, 288-90(1921).—The process is based upon reaction in the elec. furnace by which the S is in large part eliminated with the gases formed. To the fusion mixt. consisting of soda ash, C, CaO and fluxes there is added a prepn. of  $\text{MgCl}_2$  and MgO (Sorel cement) mixed with  $\text{MnO}_2$ . The addn. of the chlorinating agent is made some time before pouring of the bath. The S set free by the Cl formed from the above prepn. gives rise, in the presence of C,  $\text{CO}_2$  or Cl, to COS or to volatile oxygenated compds. of S. Dolomite, treated with Cl by Ashcroft's process, may be used instead of the mixt. of  $\text{MgCl}_2$  and MgO. The amt. of the desulfurization mixt. that should be added can best

be detd. by trial. Alumina in the form of bauxite may be added to avoid choking up of the crucible from formation of difficultly fusible slags. Phosphorite may be added to obtain cast Fe rich in P.

ROBERT S. POSMONTIER

**Two electrolytic copper processes compared.** A. G. BETTS. *Eng. Mining J.-Press* **115**, 19-21(1923).—A general theoret. discussion. The application of the diaphragm (Siemens) process is compared with the non-diaphragm process with insol. anodes. The diaphragm process is ideally fitted for treatment of non-oxidized ores (native Cu and sulfides), gives high efficiencies, and obviates troubles due to ferric salts. It consists in electrolyzing an acid sulfate soln. of Cu and ferrous Fe. C anodes are used, and proper diaphragms keep the  $\text{Fe}_2(\text{SO}_4)_3$  formed at the anode, away from the cathode. Non-diaphragm methods use insol. anodes such as Pb and although best fitted for treatment of oxidized ores, suffer from anode corrosion (due to chlorides and nitrates) and from low efficiencies due to presence of ferric Fe. For treatment of mixed sulfide and oxidized ores, a modified method consisting of both processes is suggested. In this case, an insol. anode, such as Pb, could be used in a diaphragm cell, and conditions could be so controlled as to have the proper amt. of ferric Fe in the leaching solns. and proper amt. of ferrous Fe in feed soln. to give good efficiencies.

CHAS. H. ELDRIDGE

**The effect of single impurities on the electrodeposition of zinc from sulfate solutions.** J. T. ELLSWORTH. *Trans. Am. Electrochem. Soc.* **42**, 187-202(1922).—The limiting value of each ordinary impurity in  $\text{ZnSO}_4$  soln. which will not seriously affect the cell efficiency is, in g. per l.: Cu 0.02, Mn 1.0, Fe 0.05, Sb 0.001, Co 0.012, CaO 0.7-1.0. Mn accelerates the effect of Sb; Co has an effect like Mn and Fe; Ca causes the Zn to become soft and spongy.

W. H. BOYNTON

**Technical applications of the electroosmotic process.** RYUZO AKIZAWA. *J. Chem. Ind. (Japan)* **25**, 1348-66(1922).—A review.

S. T.

**High-voltage thermionic rectifiers.** A. SCHMIDT, JR. *Gen. Elec. Rev.* **26**, 116-9 (1923).—Connection diagrams for single-phase half-wave, single-phase full-wave, 3-phase half-wave, 3-phase full-wave, and 3-phase double-Y rectifiers are given. Photographs of various types of rectifiers from the 20-watt, 400-volt to the 40-kw. 15,000-volt kenotron are reproduced.

D. MACRAE

**Autovalve lightning arrester.** A. L. ATHERTON. *Elec. J.* **20**, 107-11(1923); cf. *C. A.* **17**, 369.—The operation of lightning arresters based on the principle previously described by Slepian is discussed.

D. MACRAE

**Maintaining dielectric strength of oil.** J. A. MILLER, JR. *Elec. World* **81**, 698-9 (1923).—Expts. are described on the dehydration of transformer oil by a centrifugal separator. The method is very efficient, rapid and cheap.

C. G. F.

**Preparation of metallic uranium (MOORE) 6.** Extracting metal compounds from ores (Brit. pat. 188,865) 9.

**Storage battery.** W. P. LOUDON. U. S. 1,447,797, Mar. 6. Structural features of vent valves which automatically close when the battery is tilted.

**Storage batteries.** F. VAN DE WIEL. Can. 228,849, Feb. 20, 1923. A battery receptacle has integral internal ledges, interrupted at the place of the positive plates, and band-shaped supporting plates bridging the intervals between the parts of the ledges.

**Storage battery.** KENSHI KAWAKAMI. Japan 40,233, Oct. 6, 1921. An alloy of Pb with one or more metals of the Mg, alkali, Sn, As, or Al groups is made porous by heating nearly to the m. p. and rotating in a centrifugal machine. This gives light and durable battery plates with high efficiency.

**Storage battery grids.** W. E. HOLLAND and J. M. SKINNER. U. S. 1,447,781,

**Mar. 6.** A sheet of the grid metal, *e. g.*, a Pb alloy, is pressed into the recesses of a mold and the pressing is continued to homogenize and densify the metal.

**Coating storage battery cases.** W. E. HOLLAND. U. S. 1,447,782, Mar. 6. Battery cases are coated with superposed layers of asphalt paint and shellac.

**Storage battery.** W. E. HOLLAND and L. J. PEARSON. U. S. 1,447,783, Mar. 6. Structural features.

**Electrode suspension in storage battery cells.** F. VAN DE WIEL. Can. 228,630, Feb. 6, 1923.

**Dry battery.** SHOTARO SUZUKI and TOSHI SUZUKI. Japan 40,255, Oct. 8, 1921. A C rod is placed in the center of a box made of porous C or perforated C plate and  $MnO_2$  is filled between them. The C box is covered with cotton and inserted into a Zn box,  $NH_4Cl$  soln. is poured on the cotton and the cell is closed with asphalt; the internal resistance of the cell is low.

**Electric batteries.** T. R. COOK and P. E. NORRIS. Can. 228,770, Feb. 13, 1923. Compound for sealing electric battery. TOYOZO KAMEYAMA and GENZO SHIMAZU. Japan 40,311, Oct. 18, 1921. The compd. is a mixt. of 53% pitch, 22% asphalt and 25% grease for reducing friction. The mixt. melts at  $70-75^\circ$ ; it seals the battery airtight, does not crack in the cold and is acid-proof.

**Electrodes.** H. BARDT. Can. 228,891, Feb. 20, 1923. Electrodes for electrolytic process are produced by electrodepositing a peroxide layer on the anode surface; a substance which is inert to  $HClO_4$  is used as anode material and a soln. of  $Mn(ClO_4)_2$ ,  $Pb(ClO_4)_2$  or a mixt. of both containing an excess of  $HClO_4$  is used as electrolyte. The current density is increased when the peroxide layer is formed.

**Electrode for alkaline storage batteries.** P. GOUIN and E. ROESEL. U. S. 1,447,657, Mar. 6. See Can. 220,876 (*C. A.* 16, 3267).

**Suspension of electrode plates in the containers of electric accumulators.** F. VAN DE WIEL. Can. 228,629, Feb. 6, 1923.

**Electrolytic gas production.** E. VESME. Brit. 188,370, July 29, 1921. The output of a gas generator is increased by heating the electrolyte so as to diminish its resistance and the soly. of gases therein; an ordinary voltage is employed. The heating may be effected by steam or hot water coils or by resistances in contact with the receptacle or immersed in the electrolyte. The desired temp., such as  $50^\circ$ , may be maintained when once attained, by the electrolytic current. Cf. 1,523, 1878.

**Producing gas by the action of an electric arc.** J. U. McDONALD. U. S. 1,447,259, Mar. 6. Oil, powd. coal or similar carbonaceous material is forced with steam into a retort within which an elec. arc is maintained, so as to form a vortex the axis of which passes through the arc, to produce gas.

**Separating substances.** H. S. HATFIELD. Can. 228,625, Feb. 6, 1923. Finely divided substances, solid or liquid, are sepd. by the use of a suspension fluid the dielec. const. of which lies between those of the different substances. One or both of the electrodes in the electrostatic field may be liquid. A mixt. of nitrobenzene and paraffin oil adjusted to give the required dielec. const. may be used and with fine suspensions it may be necessary to use an agent such as neat's foot oil to produce deflocculation of the suspension. App. is specified.

**Precious metals from ores.** C. C. MCBRIDE. U. S. 1,447,140, Feb. 27. An ore of sand-like condition contg. precious metals is continuously agitated as it is passed through a soln. of  $NaCl$  in a horizontal extn. app. and is at the same time electrolyzed, using an insol. anode and a cathode of amalgamated Pb.

**Tungsten.** SIEMENS BROS. & CO., LTD and W. H. LE MARÉCHAL. Brit. 188,706, June 18, 1921. W in the form suitable for the manuf. of drawn filaments for elec. lamps, thermionic valves, etc., is obtained by incorporating a small proportion of thorium and



boric acid with the W at any stage in its production. Solns. of Th nitrate and boric acid may be added to tungstic oxide, and the mixt. dried, calcined, and reduced in H; or W oxide may be first treated with Th nitrate, dried, calcined, and reduced, and the product moistened with boric acid and heated in H.

**Electrolytic iron.** F. A. EUSTIS, C. R. HAYWARD, H. M. SCHLEICHER and D. BELCHER. Can. 228,615, Feb. 6, 1923. Sulfide ore of Fe is treated with a soln. contg. ferric Fe without free acid, thereby both reducing the soln. and dissolving Fe from the ore. The Fe is then deposited by electrolysis. The soln. is maintained at about the b. p. and the cathode may have a relatively fusible surface for ease in removing the deposit. The cathode may be depolarized by rubbing or by the ferric salts pptd. in the soln. Cf. C. A. 17, 243.

**Electrolytic iron.** F. A. EUSTIS, C. R. HAYWARD, H. M. SCHLEICHER and D. BELCHER. Can. 228,616, Feb. 6, 1923. A ferric soln. is reduced with an elec. current, an Fe ore is leached with the reduced soln. and the Fe is deposited from the leach liquor by electrolysis; thus a ferric soln. is again produced. Cf. C. A. 17, 243.

**Electrolytic smelting.** R. RODRIAN. U. S. 1,447,892, Mar. 6. The ore to be treated, *e. g.*, to recover metals, is added in finely divided condition to a melted mixt. of  $\text{NaNO}_3$  and  $\text{Na}_2\text{CO}_3$  and after addn. of metallic Pb the materials are electrolyzed.

**Lead alloys with alkaline earth metals.** W. MATHESIUS. U. S. 1,447,143, Feb. 27. Alloys of Pb with a plurality of alk. earth metals, *e. g.*, alloys contg. Pb, Ca, Ba and Sr, are prepd. by electrolysis of a fused mixt. of salts of the alk. earths required, *e. g.*, chlorides, in contact with a Pb cathode. After the fused electrolyte has attained a condition of equil., successive small portions of salts are added contg. the alk. earth metals in the proportions in which they are desired in the final alloy.

**Bath for electrolysis.** GENJIRO HIRO and SAKICHI HIRUMA. Japan 40,251, Oct. 8, 1921. The bath is a porous porcelain box having a diaphragm and the outer surface is covered with enamel.

## 5—PHOTOGRAPHY

LOUIS DERR

Size-frequency distribution of particles of silver halide in photographic emulsions and its relation to sensitometric characteristics. III. E. P. WIGHTMAN, A. P. H. TRIVELLI and S. E. SHEPPARD. *J. Phys. Chem.* 27, 1-51(1923); cf. C. A. 16, 1914, 4151.—An improved method of studying microscopically the size-frequency distribution of Ag halide in a photographic emulsion is given in detail, together with an estimate of the principal sources of error in the method. Frequency curves and data are given for a number of typical emulsions ranging from the slowest to the fastest. An exponential equation of the form  $y = y_0 e^{-Kx}$  fits some of the data very closely while for other data a Gaussian equation of the form  $y = y_0 e^{-K(x-a)^2}$  can be used to express the distribution of sizes,  $y$  being the frequency (per 1000) and  $x$  the size of grains. The distribution of total area of grains in each class per unit area of plate with the variation of class size is more important photographically than the simple frequency distribution; it is obtained by multiplying each side of the above equations by the factor  $Nx/1000$  in which  $N$  represents the total no. of grains per  $\text{cm}^2$  of the plate. Empirical sensitometric characteristics for these emulsions were also detd. and are summarized in tabular form for comparison with the frequency data. The data show definitely that relative speed of the emulsions increases rapidly with the increase of av. size and range of size of the grains contained therein. Of the other characteristics, no definite statement can be made since these depend much more on the variation of other factors in the prepn. and coating of the emulsions. IV. *Ibid* 141-66.—The existence and nature of statistical variation of sensi-

tivity among silver halide grains are discussed. A mathematical expression for photolysis in a homogeneous system is developed in relation to the density-exposure function; it has the form  $D = -\ln[e^{-D_m} + (1 - e^{-D_m})e^{-K/E}]$ . The relation of statistical variation of inertia to the density-exposure function will correspond with the inertia-variation function. Conditions permitting this correspondence are noted; if the size-frequency corresponds with the sensitivity-frequency, then the curve of "reciprocity size-frequency" gives the inertia-variation curve, and integration of this the density-exposure function. For the most general case,  $dD/D_m - D = KdE$ , where  $K = f(i)$  or a function of inertia, the integration gives  $D = D_m(i - e^{-\mu})$  in which  $\mu = D_m/K(1 - e^{-K/E})$ ,  $E$  being the exposure and  $D_m$  the max. density. E. P. WIGHTMAN

**Increasing the general sensitiveness of emulsions by means of dyes.** H. LÜPPO-CRAMER. *Phot. Ind.* 1922, 238.—Although slow emulsions have their general sensitiveness increased by treatment with various dyes, this is not the case with rapid ones unless the colloidal Ag formed during ripening has been previously dissolved in chromic acid. The superiority of colloidal Ag to dyes as a sensitizer is ascribed to the penetration of the Ag, formed during ripening, to the center of the grain, while the dye lies only on the surface. L. DERR

**Formation of silver photobromide by dyes.** H. LÜPPO-CRAMER. *Phot. Ind.* 1922, 14.—Basic dyes, such as methylene blue and tolusafranine, act as do mineral acids in coagulating mixed Ag and AgBr sol; when the excess Ag is removed by  $\text{HNO}_3$  a fine rose-red to red-violet photobromide remains. Acid dyes do not coagulate the sol, and may stabilize it. L. DERR

**Regeneration of the fixing bath.** A. STEIGMANN. *Phot. Ind.* 1922, 493.—The Ag may be recovered from a fixing bath by  $\text{Na}_2\text{S}_2\text{O}_4$  without rendering the bath alk., by adding very small amts. of safranine. The color may be removed by subsequent agitation with animal black. A bath may be regenerated 3 times without detectable difference from a new bath. L. DERR

**Toning with tin salts.** J. G. F. DRUCE. *Brit. J. Phot.* 69, 433-4(1922).—The Ag image is bleached to ferrocyanide and this is again reduced by alk.  $\text{SnCl}_2$  soln. L. DERR

**Grain structure versus light quanta in the theory of development.** W. CLARK. *Brit. J. Phot.* 69, 462-3(1922).—The developability of Ag halide grains is ascribed to the presence of reduction centers distributed according to the laws of chance and made visible by initial development. C. has produced these centers by treatment with Na arsenite soln. and finds their distribution to be the same as for light and X-rays. The results indicate that the reduction centers are an essential part of the grain structure, and that light-action is not necessary to their formation. L. DERR

**The quantum theory of photographic exposure; a criticism.** F. C. TOY. *Brit. J. Phot.* 69, 443(1922).—The conclusion of Trivelli and Righter (*C. A.* 16, 3441) is disputed on the ground that many examples are observable where only 1 grain is developed of 2 in contact. Results of Toy's recent work disagree with Silberstein's equation, and S.'s theory is claimed to be at variance with the expts. L. DERR

**Gas toning.** K. C. D. HICKMAN. *Phot. J.* 63, 110-1(1923).—Bromide prints from the wash water are fumed with gaseous Cl for 30 sec. and subjected to the draft from a fan, after which a few sec. exposure to  $\text{H}_2\text{S}$  is followed by the fan blast for 20 min. by which time the print is dry. L. DERR

**Influence of stirring on the rate and course of development.** S. F. SHEPPARD and FELIX A. ELLIOTT. *J. Franklin Inst.* 195, 211-28(1923).—With hydroquinone, pyrogallol, *p*-aminophenol and elon developers, the velocity of development was little affected by rates of flow up to 4 cm. per sec. Hydroquinone carbonate, at low stirring velocity, gave an effect like bromide depression (induction), which was removed as the stirring

velocity increased. The induction with the other developers was either small or negligible. The regression is attributed to improved removal of sol. bromide from the film with increased stirring velocity.

JOSEPH S. HEPBURN

NIETZ, A. H. **The Theory of Development.** (Photography.) Monograph No. 2 from the Research Laboratory of Eastman Kodak Co. New York: D. Van Nostrand Co. 190 pp. \$2.50.

WALL, E. J. **Practical Color Photography.** Boston: Am. Photographic Pub. Co. 248 pp. \$3.

**Photomechanical printing-surfaces.** M. DE 'SPERATI. Brit. 189,123, Nov. 13, 1922. Addn. to 162,640 (C. A. 15, 3255). In the process described in the principal patent wherein a negative is treated in a bath of  $\text{HgCl}_2$  and  $\text{NH}_3$  to make the image portions more absorbent to  $\text{H}_2\text{O}$  and more repellent to ink, and is then converted into a printing-surface by resensitizing with dichromate and exposing it from the back, the negative is treated, after exposure and washing, with a reagent, such as a soln. of I in K iodate, which imparts a clear color to the image and enables the inking operation to be controlled, and which also imparts compactness and strength to the gelatin image layer. Cf. C. A. 16, 1051.

**Sensitized photographic coating.** J. H. CHRISTENSEN. U. S. 1,447,759, Mar. 6. A celluloid sheet or other suitable support is coated with a Ag halide gelatin film of ordinarily used sensitiveness in which the Ag halide is present in such small amt. in proportion to the gelatin that the film is practically transparent and allows the light to pass through practically without any spreading.

## 6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

**Subsidiary valence. XXVI. Complexes with sulfur dioxide.** FRITZ EPHRAIM AND CLARA AELLIG. *Helvetica Chim. Acta* 6, 37-53(1923).—The absence of relation between ionizing power of a solvent and its ability to form addn. compds. is indicated by the fact that  $\text{SO}_2$ , in contrast to  $\text{H}_2\text{O}$  and  $\text{NH}_3$ , forms addn. compds. only with iodides and thiocyanates of alkali and alk. earth metals and badly defined products with Al halides. The tensions of these compds. are nearly independent of the nature of the metal ion. It is here shown that alkali metal salts of fatty acids and  $\text{BzOH}$  add  $\text{SO}_2$ , the capacity being least in formates and increasing in the order acetate, propionate, butyrate, valerate. Li salts add no  $\text{SO}_2$ , Na less well than K, Rb and Cs. The formates add: Na, 0; K, about 0.5; Rb and Cs, 1 mol.  $\text{SO}_2$ . All other compds. add 1 mol. at temps. above  $0^\circ$ . Gaseous  $\text{SO}_2$  is taken up slowly and the reaction is completed with difficulty. Liquid  $\text{SO}_2$  is preferable. The Na salts, even out of contact with air, gradually lose  $\text{SO}_2$  much as silicic acid gel loses water on aging. The K, Rb and Cs compds. are stable up to about  $80^\circ$  and loss of  $\text{SO}_2$  is accompanied by other decompn. reactions. Formates, but no other salts, decompose on heating with sepn. of S. The addn. compds. at room temp. are colorless except the formates, which are orange, like those of the alkali iodides, and impart a yellow color to the liquid  $\text{SO}_2$ . The Cs compds. are sol. in liquid  $\text{SO}_2$  but impart no color to it. The cause of the yellow color of concd.  $\text{NaHSO}_3$  solns. was investigated. It is not due to impurities as has frequently been assumed. With purest materials the color invariably developed when  $\text{SO}_2$  was led into solns. of NaOH, KOH,  $\text{NH}_4\text{OH}$  or of alkali carbonates, sulfites, bisulfites, formates, acetates and to a less degree in  $\text{Ca}(\text{OH})_2$  and  $(\text{AcO})_2\text{Zn}$ . No color developed in alkali chlorides, nitrates, sulfates, bisulfates or in alk. earth (except Ca) hydroxides or carbonates, in

Mg or Cd hydroxides or in free  $H_2SO_4$ . The color does not appear in solns. more dil. than 0.5 *N* and reaches a max. in 5 *N* solns., in which it is quite stable. It is about the tint of dil. chromate solns. and its absorption spectrum was almost identical with that of chromate soln. of the same tint. That a compd. is formed is shown by the fact that the solns. upon diln. do not follow Beer's law; a 5 *N* soln. of the K salt showed more than 10 times the color intensity of a *N* soln. The yellow compd. could not be isolated. It is certain that the  $SO_3$  content of the yellow soln. exceeds that required for the formula of bisulfite by only an inconsiderable amt.

A. R. MIDDLETON

**Perchlorates of bismuth and antimony.** FR. FICHTER AND ERNST JENNY. *Helvetica Chim. Acta* 6, 225-31(1923).—The statements of Muir (*Chem. News* 33, 15 (1876)) repeated in the handbooks, are incorrect and also dangerous. Bi can dissolve in  $HClO_4$  only in consequence of reduction of the latter to  $HClO_3$  and  $ClO_2$ , which invariably explodes if Bi powder is heated with 70% acid. The expt. is safe only with small amts. of 40% acid and careful heating. The product was found to be identical with that obtained by dissolving the oxide. The following salts were prepd. Not over 3 g.  $Bi_2O_3$  to 10 g.  $HClO_4$  dissolved slowly in small portions in 70% acid with heating to fuming after each addn. to remove water and crystn. *in vacuo* gave  $Bi(ClO_4)_3 \cdot 5H_2O$ , in small hexagonal plates, extremely reactive to water. Soln. of oxide in more dil. acid or addn. of water to the neutral salt and evapn. over  $CaCl_2$  gave  $BiOClO_4 \cdot 3H_2O$ , unstable and passing readily into  $BiOClO_4 \cdot H_2O$ , well formed rhombohedrons, the most stable of the series. On drying at 80-100° this decomposes to a white powder of the compn.  $BiOClO_4$ , the compd. reported by Muir. Contrary to M., this salt, as well as all the preceding hydrates, is sol. in water without turbidity. Freshly pptd.  $Sb(OH)_3$  in warm 70%  $HClO_4$  gave  $SbOClO_4 \cdot 3H_2O$ , well crystd. and in form like the corresponding hydrate of the Bi salt. This salt decrepitates strongly when heated above 60° with formation of higher oxides of Sb. It is at once completely hydrolyzed when placed in water.

A. R. M.

**Reduction of iodate and chlorate by arsenious acid.** HANS KUBINA. *Monatsh.* 43, 439-68(1923).—Both reactions were found to be independent of the concn. of  $H_2AsO_3$ . The reduction of chlorate did not take place in presence of  $H_2SO_4$  but proceeded smoothly in HCl soln. Kinetic measurements established that the primary reaction is of the first order and is  $XO_3 + X' \rightarrow A$  (measurable) where A is probably HIO and  $HClO_3$ , resp. The iodate reduction showed strong acceleration at the beginning, iodide ion acting as catalyzer and the catalyzed reaction being found of the second order. The following reactions are believed to take place:  $ClO_3^- + Cl^- + 2H^+ \rightarrow H_2ClO_3 + Cl$  (measurable);  $H_2ClO_3 + 4Cl^- + 4H^+ \rightarrow 5Cl + 3H_2O$  and  $3Cl_2 + 3AsO_3^{---} + 3H_2O \rightarrow 3AsO_4^{---} + 6Cl^- + 6H^+$  (rapid).  $IO_3^- + 2I^- + 2H^+ \rightarrow HIO + 2IO^-$  (measurable);  $2IO^- + 2AsO_3^{---} \rightarrow 2AsO_4^{---} + 2I^-$  and  $HIO + AsO_3^{---} \rightarrow AsO_4^{---} + H^+ + I^-$  (rapid). For the latter the velocity is given by  $dx/dt = [K_1 + K_2[I]^{1/2}[IO_3^-]][H^+]$ . Neither  $Cl_2$  nor  $ClO_2$  could be detected in the solns. of  $ClO_3$ . A. R. M.

**Polynuclear acetato and formato cations of barium and cerium.** R. WEINLAND AND A. HENRICHSSEN. *Ber.* 56B, 528-38(1923); cf. *C. A.* 17, 34.—Complex cations, analogous to those previously described contg. Pb, are formed by Ba and, surprisingly, by  $Ce^{II}$ . The salts below were obtained generally by treating the acetate of the metal with the acid contg. the desired cation. A few could be obtained by double decompn. (A) Salts of  $[Ba_2(AcO)_2]_2$ :  $(NO_3)_2 \cdot 8H_2O$ ;  $ClO_4 \cdot AcO$ ;  $(ClO_4)_2 \cdot 2AcOH$ ; picrate $_2 \cdot H_2O$ ;  $ClO_4 \cdot AcO$ . (B) Salts of  $[Ba_3(HCO_2)_2]_2$ :  $(NO_3)_2 \cdot 2H_2O$ ;  $ClO_4 \cdot HCO_2 \cdot H_2O$ ; picrate $_2 \cdot 4H_2O$ ;  $[Fe(CN)_5NO] \cdot 6H_2O$ ;  $[Fe(CN)_6] \cdot 10H_2O$ ;  $[Co(CN)_6] \cdot 2HCO_2K \cdot 8H_2O$ ; also  $[Ba_2(HCO_2)_2]_2 \cdot [Fe(CN)_6] \cdot 2HCO_2K \cdot 8H_2O$ . (C) Salts of  $[Ce_3(AcO)_3]_2$ :  $(ClO_4)_2 \cdot (AcO)_4 \cdot 12H_2O$ ; picrate $_3 \cdot (AcO)_3 \cdot 3H_2O$ ;  $(NO_3)_2 \cdot 13H_2O$ ;  $(C_2O_4)_2 \cdot 6H_2O$ ;  $2[Ce_3(AcO)_3]Cl_2 \cdot (AcO)_4 \cdot Ce(AcO)_3 \cdot 28H_2O$ . These salts are generally well crystd.; they are easily sol. in water and can be recrystd.

from it undecompd. and are stable in air. The Ce picrate is orange-red; the chromate is microcryst. and only slightly sol. in water but readily sol. in mineral acids. Dehydration of the Ce salts indicated that at least 3 mols.  $H_2O$  are in the complex cation. The formulation of the cations rests chiefly on analogy to the Pb salts. The ready formation of these cations leads to the deduction that a soln. of  $Ba(AcO)_2$  contains  $[Ba_2(AcO)_3]-(AcO)_2$ .  
A. R. MITDLINGTON

**Dissembling power of condensed green chromic sulfate.** (Complex ion formation with polymerized chromic sulfate.) A. RECOURA. *Bull. soc. chim.* 33, 67-71 (1923); cf. *Ann. chim. phys.* 4 (1895).—Colson (*Ann. chim. phys.* 12, 98) has established that, immediately after its soln. in water, chromic sulfate exists as  $[Cr_2(SO_4)_3]_2$  and that if this soln. is preserved at about  $0^\circ$  it depolymerizes slowly and at the end of about 24 hrs. the depolymerization is complete. But all the sulfuric acid is still in the complex; the change in soln. continues and a little later  $SO_4$  ions can be detected in soln. R. has shown that while  $Cr_2(SO_4)_3$  in the simple form can "dissemble" three mols. of metallic sulfate, in its condensed form,  $[Cr_2(SO_4)_3]_2$ , one mol. can "dissemble" hundreds of mols. of metallic sulfate. A soln. of 1 mol. of the green sulfate, 140 mols.  $K_2SO_4$  and 140 mols. benzidine was quickly made up so that the soln. was 0.005 *N* in  $K_2SO_4$  and 0.1 *N* in  $HNO_3$ . The soln. was kept at  $0^\circ$  for 30 min. and agitated energetically from time to time and then the amt. of benzidine sulfate pptd. was detd. On repeating the expt. with solns. of green sulfate of increasing age the results showed the following ratios for the number of mols. of  $K_2SO_4$  "dissembled" per mol. of the green sulfate: 0 hrs., 68; 2 hrs., 41; 5 hrs., 27; 8 hrs., 19; 24 hrs., 9; 3 days, 0. Since according to the measurements of Colson the depolymerization is complete at the end of 24 hours, these figures indicate the effect of the degree of polymerization of the sulfate on its "dissembling power." In another expt. 2400 mols. of  $K_2SO_4$  were "dissembled" by one mol. of the condensed green sulfate so that they were not pptd. by  $BaCl_2$  at the end of 5 hrs. When the soln. of the green sulfate was three days old all the  $K_2SO_4$  could be pptd. by  $BaCl_2$ .  
D. MACRAE

**Some complex salts of copper and thallium.** G. CANNERI. *Gazz. chim. ital.* 52, II, 266-70 (1922).—The complexes of Cu belong to the large group of imperfect complexes. Their solns. are the seat of mobile equil. due to more or less profound hydrolytic dissocn. Numerous addn. compds. of Cu and the corresponding alkali salts are known. The index of coördination in these compds. seems to become more definite when the salts involved are less sol. Such complexes of Tl salts were prepd. On mixing satd. solns. of  $Tl_2SO_4$  and  $CuSO_4$  bright blue crystals of *cupric thallium sulfate*,  $Tl_2Cu(SO_4)_2 \cdot 6H_2O$ , sep'd. It is also pptd. by adding  $HCl$  to the concd. soln. This salt is strictly analogous to  $K_2Cu(SO_4)_2 \cdot 6H_2O$ , for which the transport no. of Cu is less than that of  $CuSO_4$  (Rieger, *Z. Elektrochem.* 7, 863 (1901)). This indicates that these salts are  $[Cu(SO_4)_2]K_2$  and  $[Cu(SO_4)_2]Tl_2$ , resp. A soln. of  $Tl_2SO_4$  added to a soln. of  $CuSO_4$  pptd. *cupric thallium sulfate* (A),  $Tl_2Cu(SO_4)_2$ , as a yellow powder. It was also obtained in 3 other ways. Concd.  $CuSO_4$  soln. +  $Tl_2CO_3$  treated with  $SO_2$  gave A and on prolonged action of  $SO_2$  a red microcryst. salt, *cuprous cupric thallium sulfate*,  $CuSO_4 \cdot 3Cu_2SO_4 \cdot Tl_2SO_4$ , in which the  $Cu^{II}$  comes to equil. with the oxidizable  $SO_2$  ion by being partly reduced to  $Cu^I$ .  $Tl_2S_2O_8$  freshly prep'd. was digested with a  $CuSO_4$  soln. contg.  $Na_2S_2O_5$ . The light white ppt.  $Tl_2S_2O_8$  is transformed gradually into a heavy microcryst. powder of *cuprous thallium thiosulfate*,  $Tl_4Cu_2(S_2O_3)_3$ , which does not decompose in warm  $H_2O$  but gives  $Cu_2S$  when treated with acids. Complexes with  $Cu_2S_2O_3$  are unknown because of the reducing power of  $S_2O_3$  on  $Cu^{++}$  ions.  
E. J. WITZEMANN

**The composition of potassium chloroplatinate.** A. VÜRTHEIM. *Chem. Weekblad* 17, 637-40 (1920).—In the estn. of K as chloroplatinate, it has been found that the compn. of the salt does not correspond with that required by the formula  $K_2PtCl_6$ .

In view of the various factors suggested by different workers on the subject, the matter has been reexamined. For the prepn. of the double salt, dil. solns. of the two pure salts were used, to avoid the difficulties in drying introduced by enclosed mother liquor, where the solns. are too strong. The soln. was then evapd. at 90° until it became sirupy, the crystals being washed free from  $\text{PtCl}_4$  with 96% alc. Drying for two hrs. at 150° was found to give const. wts. By using a const. quantity of the KCl soln. with a slight excess of  $\text{PtCl}_4$ , practically const. yields of the double salt were obtained. Pt and Cl were detd. in each sample, the K being known from the quantity of KCl soln. taken. The mean of six concordant detns. gave K : Pt : Cl = 15.98 : 40.32 : 43.16, the formula  $\text{K}_2\text{PtCl}_6$  requiring, the latest at. wts. being used, 16.09 : 40.15 : 43.76. Quantities of the double salt were recrystd. and dried under various conditions, and it was found that by pptn. from aq. soln. by means of alc., the salt was obtained absolutely free from water, drying at 110° being as effective as drying at 150° in arriving at const. wts. The compd. so treated gave on analysis K : Pt : Cl = 16.09 : 40.63 : 43.51, which, although much nearer to the theoretical than the above results, still shows some deviation. The accuracy of the accepted at. wt. of Pt is questioned, and the variations in this const., as accepted in the last 20 years, are pointed out. J. C. S.

A crystallographic study of some complex compounds of iridium and rhodium. A. DUFFOUR. *Bull. soc. franc. mineral.* 45, 48-61 (1922).—D. describes the crystallography and some of the optical properties of:  $d\text{-K}_3\text{IrCl}_6(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ , orthorhombic,  $a : b : c = 1.215 : 1 : 1.528$ ;  $l\text{-K}_3\text{IrCl}_6(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ , ortho,  $1.220 : 1 : 1.536$ ;  $\text{K}_3\text{IrCl}_6(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$ , (A) triclinic form,  $a : b : c = 1.2572, \alpha 89^\circ 52', \beta 101^\circ 35', \gamma 90^\circ 40'$ ; (B) monoclinic form,  $0.874 : 1 : 0.523, \beta 95^\circ 54'$ ;  $\text{K}_3\text{Ir}(\text{C}_6\text{H}_5\text{N})_2\text{Cl}_4(\text{C}_2\text{O}_4)_2 \cdot 1.5 \text{H}_2\text{O}$ , orthorhombic,  $0.7926 : 1 : 1.383$ ;  $\text{NH}_4\text{Ir}(\text{C}_6\text{H}_5\text{N})_2\text{Cl}_4 \cdot \text{H}_2\text{O}$ , monoclinic,  $1.192 : 1 : 0.644, \beta 94^\circ 33'$ ;  $\text{KIr}(\text{C}_6\text{H}_5\text{N})_2\text{Cl}_4 \cdot \text{H}_2\text{O}$ , monoclinic,  $1.169 : 1 : 1.439, \beta 97^\circ 54'$ ;  $\text{NH}_4\text{Ir}(\text{C}_6\text{H}_5\text{N})_2\text{Cl}_4 \cdot \text{H}_2\text{O}$ , monoclinic,  $a : b : c = 1.416, \beta 99^\circ 24'$ ;  $\text{KIr}(\text{C}_6\text{H}_5\text{N})_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , monoclinic,  $1.198 : 1 : 1.304, \beta 123^\circ 59'$ ;  $2\text{K}_3\text{Rh}(\text{C}_2\text{O}_4)_3 \cdot \text{KCl} \cdot 8\text{H}_2\text{O}$ , rhombohedral,  $c = 0.9179$ ;  $2\text{K}_3\text{Ir}(\text{C}_2\text{O}_4)_3 \cdot \text{KCl} \cdot 8\text{H}_2\text{O}$ , rhombohedral,  $c 0.91150$ . E. F. H.

Some properties of manganese dioxide. A. DE HEMPTINNE. *Bull. acad. roy. Belg.* 8, 71-5 (1922).— $\text{MnO}_2$  is reduced by H or a mixt. of H and  $\text{H}_2\text{O}$  at ordinary temps., and at atm. pressures. After 5 days a rapid and progressive reduction in pressure due to absorption of H was perceptible ( $\text{P}_2\text{O}_5$  was used to absorb the water formed), and after 53 days about  $\frac{1}{3}$  of the H had been used up. The reduced product was rapidly re-oxidized on exposure to the air. When  $\text{MnO}_2$  was exposed, similarly, to a mixt. contg. 33% of  $\text{H}_2\text{S}$  and 67% of H a considerable diminution in vol. took place in 3 mins., the  $\text{MnO}_2$  being converted into a S compd. from which  $\text{H}_2\text{S}$  was evolved on treatment with  $\text{H}_2\text{SO}_4$ . J. S. C. I.

The solubility of halides of univalent copper in sodium thiosulfate. G. CANNIERI AND R. LUCHINI. *Gazz. chim. ital.* 52, II, 261-6 (1922).—That the halides of  $\text{Cu}^I$  are sol. in alkali thiosulfates has long been known (1866) and 4 previous workers have described complexes obtained in this way in which the general reaction  $2\text{CuX} + 2\text{M}_2\text{S}_2\text{O}_3 \rightarrow \text{Cu}_2\text{S}_2\text{O}_3 + \text{M}_2\text{S}_2\text{O}_3 + 2\text{MX}$  takes place.  $\text{Na}_2\text{S}_2\text{O}_3$  fuses at 56° giving a supersatd. soln. Such a soln. was treated with excess fresh  $\text{Cu}^I$  halide (from  $\text{Cu}^{II}$  halide +  $\text{SO}_2$ ) in which it dissolved freely. This pasty mass was dissolved in the minimum of  $\text{H}_2\text{O}$ , freed from excess  $\text{Cu}^I$  halide and placed in a vacuum desiccator over  $\text{H}_2\text{SO}_4$ . White microcrystals sepd. and were filtered off and washed with  $\text{EtOH}$ . These salts decompose on heating, giving  $\text{SO}_2$ , and give limpid colorless solns. in  $\text{H}_2\text{O}$ . Dil  $\text{HNO}_3$  decomposes them, giving  $\text{Cu}_2\text{S} + \text{SO}_2 + \text{H}_2\text{S}$ . Conc'd. cold  $\text{HNO}_3$  gives  $\text{Cu}(\text{NO}_3)_2 + \text{S}$ .  $\text{HCl}$  does not act upon them.  $\text{NH}_4\text{OH}$  slowly oxidizes them at the surfaces, giving blue  $\text{Cu}^{II}$  ions.  $\text{KOH}$  slowly ppts. yellow  $\text{CuOH}$ .  $\text{K}_4\text{Fe}(\text{CN})_6$  slowly ppts. the  $\text{Cu}^I$  deriv.  $\text{KCNS}$  gives no ppt. with these  $\text{Cu}^I$  salts. Cu was detd. electrolytically. Na was

dett. in the electrolyzed soln. as  $\text{Na}_2\text{SO}_4$  after the Cu was removed.  $\text{S}_2\text{O}_3$  was detd. both gravimetrically and volumetrically by methods described. The  $\text{H}_2\text{O}$  of crystn. could not be detd. accurately. The salts obtained and analyzed were:  $\text{CuCl} \cdot 5\text{Na}_2\text{S}_2\text{O}_3$ ;  $\text{CuBr} \cdot 5\text{Na}_2\text{S}_2\text{O}_3$ ;  $\text{CuBr} \cdot \text{Cu}_2\text{S}_2\text{O}_3 \cdot 9\text{Na}_2\text{S}_2\text{O}_3$ ;  $\text{Cu}_2\text{S}_2\text{O}_3 \cdot 5\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{NaI}$ ;

$2\text{CuCNS} \cdot 5\text{Na}_2\text{S}_2\text{O}_3$ . The following structures:  $\left[ \text{Cu} \begin{smallmatrix} \text{Cl} \\ (\text{S}_2\text{O}_3)_5 \end{smallmatrix} \right] \text{Na}_{10}$ ;  $\left[ \text{Cu} \begin{smallmatrix} \text{Br} \\ (\text{S}_2\text{O}_3)_5 \end{smallmatrix} \right] \text{Na}_{10}$ ;  $\left[ \text{Cu} \begin{smallmatrix} \text{I} \\ (\text{S}_2\text{O}_3)_6 \end{smallmatrix} \right] \text{Na}_{11}$ ;  $\left[ \text{Cu} \begin{smallmatrix} \text{CNS} \\ (\text{S}_2\text{O}_3)_5 \end{smallmatrix} \right] \text{Na}_{10}$  might be assigned by analogy with formulas given by Werner to the similar compds. obtained with  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  by Rosenheim and Steinhauser (*Z. anorg. allgem. chem.* 25, 103(1901)). Such hypothetical formulas are not supported experimentally except by the color of the salts, which suggests that the  $\text{Cu}^1$  ion is contained in a complex in which it is more resistant to reagents, but the dissociating power of  $\text{H}_2\text{O}$  on them does not permit of making any phys. measurements.

E. J. WITZERMANN

**Catalytic hydrogenation of sulfur dioxide.** MARGARET G. TOMKINSON. *Compt. rend.* 176, 35-6(1923).—A mixt. of  $\text{SO}_2$  with H, held at  $280^\circ$  for 24 hrs., does not react, but at red heat gives  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and S; nascent H reacts more readily (cf. Berthelot, *Ann. chim. phys.* [7] 14, 289(1898)). When  $\text{SO}_2$  and dry H are passed over finely divided Ni, prepd. by heating the oxalate in H at  $280^\circ$ , there is no reaction below  $280^\circ$ ; above this temp. a little  $\text{H}_2\text{O}$  vapor first appears, increasing in amt. at  $350^\circ$  with formation of a little  $\text{H}_2\text{S}$ , and followed at  $400\text{--}50^\circ$  by free formation of  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , and S. With slow passage of the gases the reaction is quant.; the catalyst eventually becomes transformed entirely into NiS, but remains active. NiS prepd. either by treating a soln. of  $(\text{AcO})_2\text{Ni}$  with  $\text{H}_2\text{S}$ , or by passing  $\text{H}_2\text{S}$  over NiO at  $200^\circ$ , is itself an active catalyst of this reaction, effective above  $300^\circ$ , but without action on propane at  $100\text{--}260^\circ$ , or on  $\text{CO}_2$  at  $300^\circ$ . CoS, and less effectively FeS, also catalyze the reduction of  $\text{SO}_2$ , but CuS and CdS are inactive. Cf. C. A. 8, 3111.

A. R. ALBRIGHT

**Recovery of osmium from microscopical preparations.** O. BOSSE AND H. VON WARTENBERG. *Z. wiss. Mikros.* 38, 346-9(1922).—The material is saponified with KOH, evapd., and the soap fused with  $\text{KNO}_3$  in a Ni crucible. The melt is treated with water, and  $\text{NiSO}_4$  soln. added. On standing  $\text{Ni}(\text{OH})_2$ , part of which becomes oxidized to the hydrated peroxide, settles out carrying with it the Os. The ppt. is filtered off, and the ppt. and filter are transferred to a 250-cc. flask fitted with a ground-in dropping funnel and provided with a drain tube. The ppt. is treated with a mixt. of  $\text{H}_2\text{CrO}_4$  and  $\text{H}_2\text{SO}_4$  and kept warm. The contents of the flask are then steam-distd., and a soln. of pure  $\text{OsO}_4$  is obtained. An iron crucible cannot be used because too much iron passes into soln. during fusion, producing an inconvenient amt. of hydroxide. In the authors' expts. 70% of the Os was recovered.

J. S. C. I.

**Preparation of metallic uranium.** R. W. MOORE. *Trans. Am. Electrochem. Soc.* 43 (Preprint); 3 illus.—Metallic U is best prepd. by converting the oxide to chloride, followed by sublimation and reduction. Reduction by Na takes place in a steel bomb in a vacuum. The sintered mass, contg. besides U, NaCl, Na and possibly traces of  $\text{UCl}_4$  and  $\text{U}_3\text{O}_8$ , is purified by successive treatment with absolute  $\text{EtOH}$ , water, and 2%  $\text{AcOH}$ . The acid is washed out by water, and the residue treated with acetone and dried in vacuum. An elec. arc method of fusing the metal to form buttons which may be rolled into thin sheets is described. The U so produced has the appearance of polished Fe, oxidizes readily and is very ductile.

W. H. BOYNTON

**Application of Scheele's reaction to preparation of potassium hydroxide.** W. DOMINIK. *Przemysl Chem.* 6, 25-36(1922).—The reaction  $2\text{KCl} + 4\text{PbO} + \text{H}_2\text{O} \rightleftharpoons \text{PbCl}_2 + 3\text{PbO} + 2\text{KOH}$  was studied by using mixts. contg. not more than 20 g. of PbO per 100 cc. of KCl soln., filtering when the reaction was complete, adding a further quantity of PbO to the filtered liquid, and repeating these operations until equil. was

attained. It was found that to obtain 1 g. of KOH about 16 g. of PbO is necessary. At the ordinary temp. the equil. between KOH and KCl may be expressed by the equation:  $K = \text{KOH/KCl} = \{1/(0.422 + 0.074[\text{OH}])\} - 1$ , and the max. concentration attainable is 112 g. KOH per l. Regeneration of PbO by treatment of the  $\text{PbCl}_2$  formed with milk of lime or  $\text{CaHCO}_3$  is not practicable, but may be accomplished by treatment with  $(\text{NH}_4)_2\text{CO}_3$  in presence of excess of  $\text{CO}_2$ , whereby  $\text{NH}_4\text{Cl}$  and  $\text{PbCO}_3$  are formed, and the latter can be converted into PbO by treatment with steam at  $300^\circ$ . With this method of regeneration the process as a whole becomes technically sound.

J. S. C. I.

**Preparation of anhydrous tin tetrachloride.** H. J. TAVERNE. *Chem. Weekblad* 17, 610(1920).—The method employed by Hensgen (*Rec. trav. chim.* 9, 303-4) for the prep. of  $\text{SbCl}_3$  is applied to tin. Cl which has been dried by passing through  $\text{H}_2\text{SO}_4$  and  $\text{CaCl}_2$  in succession is passed over granulated tin, contained in a tube about 40 cm. in length and 2 cm. in diam., which is supported in an inclined position in an elementary-analysis furnace. The tube is connected at its lower extremity with an adapter piece, which fits through a cork in the neck of a distn. flask, the arm of which is connected to a  $\text{CaCl}_2$  tube. The chloride trickles down the tube, and collects as a yellow fluid in the flask, while the impurities in the tin remain behind in the tube. The chloride is afterwards redistilled, with the usual precautions.

J. C. S.

Reduction of  $\text{CaSO}_4$  and  $\text{MgSO}_4$  by CO, C and  $\text{H}_2\text{S}$  (ZAWADZKI, *et al.*) 18. Crystal structure of natural and synthetic oxides of uranium, thorium and cerium (GOLDSCHMIDT, THOMASSEN) 8.

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## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

**The report of A.O.A.C. referee on nitrogen.** H. S. BAILEY. *Cotton Oil Press* 6, No. 9, 37-8(1923).—An abstr. of the report by I. K. Phelps as referee on Nitrogen, to the 1922 meeting of the A.O.A.C. The directions sent to collaborators for the study of the Devarda Alloy method for the detn. of N in nitrates are given in full. From a study of the results of 23 chemists P. concludes that 1 hr. is sufficient time for distn., and the agreement among different analysts is so satisfactory the method should be studied next year on com. nitrates. The use of  $\text{Na}_2\text{S}_2\text{O}_3$  as a precipitant for Hg in the Moore method should be studied as a substitute for  $\text{K}_2\text{S}$  or  $\text{Na}_2\text{S}$  in the Kjeldahl method.

H. S. B.

**Analysis by temperature changes.** D. M. STRICKLAND. *Metal Ind.* 20, 339-40 (1922).—The thickness of the Zn coating on galvanized articles can be detd. by measuring the rise in temp. caused by the soln. of the Zn from a definite area of the sample in a definite vol. of concd. HCl. The rise in temp. multiplied by an experimentally obtained



conversion factor gives the wt. of the Zn on the sample. The detn. can be made in a glass vessel. The temp. must be read from a thermometer graduated in 0.1°.

F. P. FLAGG

**Alkalimetric determination of magnesium and calcium salts.** R. WILLSTÄTTER AND E. WALDSCHMIDT-LEITZ. *Ber.* 56, 488-91 (1923).—If a slight excess of 0.1 N NaOH is added to a soln. of a Mg salt and then enough alc. is added to make the soln. contain 66-75% alc., the excess of NaOH can be titrated by acid, with 10 drops of 0.5% alc. thymolphthalein as indicator for each 100 cc. of liquid. Ca can be titrated similarly if, instead of alc., enough acetone is added to make a mixt. contg. 85-90% acetone. In a soln. contg. both Ca and Mg, the Mg alone can be titrated by using alc. to decrease the soly. of  $Mg(OH)_2$  and then in another portion of the soln. the Ca and Mg together can be detd. by using acetone to keep both  $Mg(OH)_2$  and  $Ca(OH)_2$  insol. In dolomite analysis, if the Fe is in the bivalent condition it will titrate with Mg. Or, if the Fe is removed by the usual pptn. with  $NH_4OH$ , the above method can be used after the removal of  $NH_4$  salt by ignition.

W. T. H.

**Potentiometric titration of arsenic and antimony.** E. ZINTL AND H. WATTENBERG. *Ber.* 56, 472-80 (1923).—One of the most satisfactory methods for titrating As or Sb is the oxidation from the 3-valent to 5-valent condition by  $KBrO_3$  in HCl soln. When the end-point is reached the bromate begins to liberate  $Cl_2$ , which bleaches methyl orange. The titration can be followed electrometrically and the same end-point is obtained. In titrating As in the presence of 5-20% HCl a sharp rise in the e. m. f. is obtained with 1 drop of 0.1 N  $KBrO_3$  at the end. The e. m. f. is the same with either acid concn. but the jump is more marked with the more dil. acid. The reaction is also very sharp in titrating Sb but the results all indicate that the old value 121.8 for the at. wt. of Sb is much nearer the truth than the value 120.2, which has been assumed correct since 1902. When both As and Sb are present in the 3-valent condition, they can be titrated together. Then the Sb can be reduced by a slight excess of  $TiCl_3$  soln. under electrometric control in 5% HCl, and the excess oxidized in the air with the aid of a little Cu salt as catalyzer. Then the  $KBrO_3$  titration will give the Sb alone.

W. T. H.

**The rapid determination of potash in acid-insoluble silicates.** Addendum. M. M. GREEN. *Ind. Eng. Chem.* 15, 429 (1923).—Additional references are given. See C. A. 17, 501.

H. G.

**Determination of potassium as bitartrate by the method of Przibylla.** I. Application of this method to potash salts from Alsace. P. HUBERT. *Ann. chim. anal. chim. appl.* 5, 9-14 (1923).—It is possible to det. K in a salt by a proximate method based upon the titration of the filtrate from the  $KHC_4H_4O_6$  ppt. with 0.1 N NaOH. It is necessary to establish first a curve by working with pure K salt to det. what wt. of K or  $K_2O$  corresponds to each cc. of NaOH used in the final titration. It is advisable to make 7 such tables: (I) General table for salts contg. 6-63%  $K_2O$ . (II) Salts contg. 12-18%  $K_2O$ . (III) Salts contg. 15-26%  $K_2O$ . (IV) Salts contg. 24-35%  $K_2O$ . (V) Salts contg. 35-45%  $K_2O$ . (VI) Salts contg. 45-55%  $K_2O$ . (VII) Salts contg. 55-63%  $K_2O$ . Such tables prepd. by taking about 25 samples for each case give good results in practice. In the analysis it is proposed to run first a preliminary test to see in which class the substance belongs and then make a final analysis with a little more care with carefully regulated vols. of the original soln. and of reagents. Of the original, finely powdered salt, weigh out 25 g. and make up the soln. to exactly 250 cc. keeping the temp. at 18° and finally filtering if necessary. For the preliminary test, take 20 cc. of this soln., add 20 cc. of 1.5 N  $Na_2C_4H_4O_6$  and 20 cc. of 1.5 N  $H_2C_4H_4O_6$  and agitate at 18° for 10 mins. Filter and take 20 cc. of the filtrate for the titration. In the final analysis, use 25 cc. of the original soln. and vary the amts. of  $Na_2C_4H_4O_6$  and of  $H_2C_4H_4O_6$  according to the values found in the preliminary titration. Use 3.2 cc. of each soln. for Class II, 9 cc.

for Class III, 12.5 cc. for Class IV, 16.7 cc. for Class V, 20 cc. for Class VI and 24 cc. for Class VII. Shake 20 mins. at 18° to effect pptn. and take 20 cc. of filtrate if the preliminary test indicated less than 26%  $K_2O$  and 25 cc. if the test indicated 26% or more. Obviously such a method of analysis is useful when a great many analyses have to be made every day.

W. T. H.

**Volumetric determination of copper by means of sodium nitroprusside.** G. JORET. *Ann. fals.* 16, 47(1923).—J.'s method (*C. A.* 17, 248) is based on the same principle as that of Zuccari (*C. A.* 9, 771), but the latter titrates directly with Na nitroprusside, with  $(NH_4)_2S$  as outside indicator. J. compared the two methods and obtained concordant results.

A. P.-C.

**New method for the determination of cadmium.** R. CERNATESCO. *Bull. sec. sci. acad. Roumaine* 8, 43-6(1922).—A study of the soly. products of  $Ag_2S$  and  $CdS$  shows that the addition of  $AgNO_3$  soln. to suspended  $CdS$  in water should convert the  $S$  into  $Ag_2S$ . If the amt. of  $Ag$  added is known, the excess can be titrated by the Volhard method with  $NH_4CNS$  soln., and thus the  $Cd$  content detd. Expts. show that an accurate analysis can be made in this way. After pptg. the  $Cd$  as  $CdS$  by bubbling  $H_2S$  into the hot soln., remove the excess of precipitant by boiling until a drop of the soln. will not darken  $(AcO)_2Pb$  paper. Then add a measured vol. of standard  $AgNO_3$  soln., warm a short time, filter and titrate with standard  $NH_4CNS$ . The soln. of  $Cd$  should not contain any chloride and the Volhard titration does not work as well in the presence of  $H_2SO_4$ . When  $HCl$  or  $H_2SO_4$  is present, therefore, it is advisable to filter off the  $CdS$  upon an asbestos filter and then throw the filter and ppt. into water for the treatment with  $AgNO_3$ . Mann has proposed a somewhat similar method for the detn. of  $Zn$ , adding  $AgCl$  to a ppt. of  $ZnS$  suspended in water, filtering and detg. the chloride that has gone into soln. Accurate results were obtained by applying the method to the analysis of  $Cd$ . It was pptd. as sulfide, the  $CdS$  was treated with  $AgCl$  and filtered. The chloride was then detd. volumetrically by the Volhard method and it was also pptd. and weighed as  $AgCl$ .

W. T. H.

**Volumetric determination of hydrogen sulfide in alkaline solution by potassium ferricyanide.** SATOYASU IIMORI. *Japan J. Chem.* 1, 43-54(1922).—The detn. depends upon the reaction between  $K_2S$  and  $K_3Fe(CN)_6$  to form  $S$  and  $K_4Fe(CN)_6$ , with Na nitroprusside as indicator. Alkali concns. of 0.05 to 0.13 molar should be used for sulfide concns. of 0.003 to 0.03 molar. Best results are obtained in volumes of about 150 cc. and carrying out the titration rapidly. The presence of sulfites and thiosulfates does not interfere with the detn. The method is also advantageous in that the detn. can be carried out in relatively concd. solns.

C. J. WESS

**Silicon in aluminium.** R. GUERIN. *Ann. chim. anal. chim. appl.* 5, 4-8(1923).—Si and Fe constitute the 2 most important impurities of commercial Al. In France the metal is classed thus; (1) more than 99.5% Al, (2) between 99 and 99.5% Al, (3) 98-99% Al. The French official method of analysis provides for the detn. of Si, Fe and Al. For the Si detn., 2 g. of metal are dissolved in 50 cc. of a mixt. contg. 1 pt. concd.  $HNO_3$ , 3 pts. concd.  $HCl$  1 pt. concd.  $H_2SO_4$  and 5 pts. water. The soln. is evapd. to fumes, dild., filtered and the residue weighed. The purity of the  $SiO_2$  is detd. by treatment with  $HF$  and  $H_2SO_4$ . For the Fe detn., 2 g. of metal are dissolved in 50 cc. of 6  $N$   $HCl$  and a titration is made by the Zimmermann-Reinhardt method.  $Al_2O_3$  is detd. by volatilizing the metal in a current of  $Cl_2$ , weighing the residue of  $Al_2O_3$ , burning off  $C$  and weighing again. The equil. diagram of Al-Si indicates, contrary to some previous assumptions, that Si exists not as a compd. but either as free Si or in solid soln. The max. amt. of Si in solid soln. is 1.5%. By the process of Pacz, excess Si is left in a finely divided, graphitoidal condition. Si in solid soln. is decomposed by acids giving  $SiO_2$  but graphitoidal Si is only dissolved by a mixt. of  $HNO_3$  and  $HF$ . It is proposed,

therefore, to det. the so-called *combined* Si, which is really in solid soln., by treating according to the above official method for the detn. of Si. Then to det. *free* Si, treat the residue from the HF and  $\text{H}_2\text{SO}_4$  treatment with 1 cc. of HF and a little  $\text{HNO}_3$  added drop by drop till no more red fumes are evolved. Then after calcining again, this second loss in wt. will correspond to the graphitoidal or free Si. To det. the *total* Si, which should be the same as the sum of the free Si and graphitoidal Si, treat the metal as in the official Si detn. but instead of treating with HF fuse with  $\text{Na}_2\text{CO}_3$  and treat the melt with water first and then add  $\text{H}_2\text{SO}_4$  little by little. Evap. to fumes, dil., filter, ignite the impure  $\text{SiO}_2$ , weigh, and volatilize by treatment with HF and  $\text{H}_2\text{SO}_4$  in the usual way.

W. T. H.

**The use of phosphorus in gas analysis.** A. HOLMES. *Ind. Eng. Chem.* **15**, 357 (1923).—A plea for the use of P rather than pyrogallol as absorbent in the detn. of  $\text{O}_2$  in gas mixts.

W. T. H.

**Determination of small quantities of molybdenum in tungsten.** W. J. KING. *Ind. Eng. Chem.* **15**, 350-4 (1923).—From 0.01 to 0.05% Mo is present in most samples of W and it is desirable to be able to det. these small quantities. A suitable colorimetric method is described which is based upon the color developed by reduced Mo in contact with a thiocyanate and extn. of this red  $\text{Mo}(\text{CNS})_3$  with ether.

W. T. H.

**The determination of bismuth.** KÖSTER. *Chem.-Zig.* **47**, 22 (1923).—In cupelling Pb contg. Bi, a dark brown spot is left in the middle of the cupel after all of the Pb has been removed. If this spot is moistened with dil. HI a bright red ring is produced and by comparing the size and extent of the ring with rings produced similarly by known amts. of Bi, an estimate of the Bi content can be made. An ore, therefore, can be assayed for Bi by fusing it with  $\text{PbO}$ , and a reducing flux, finally cupelling the Pb button and testing as above.

W. T. H.

**The determination of silicon in iron.** E. STAUDT. *Chem.-Zig.* **47**, 87 (1923).—Dissolve 4.69 g. of sample in 40 cc. concd. HCl. When action is over, add 5 cc. concd.  $\text{HNO}_3$  dropwise, boil, dil. with 40 cc. of hot water and filter. Wash the siliceous residue with 10%  $\text{HCl}$  and calcine at  $900^\circ$ . Weigh and multiply by 10.2 to get the % Si. This method of analysis with the correction factor of 2% gives good results in the analysis of cast Fe but the values are low for wrought Fe.

W. T. H.

**Selection of cast-iron samples.** LUIGI LOSANA AND CARMELO CIMINO. *Giorn. chim. ind. applicata* **4**, 521-5 (1922).—This study was carried out to exam. the distribution of the various constituent elements in cast irons on the basis of the subdivision of the sample. Borings of cast irons of various compns. were made under identical mech. conditions. Series of complete analyses were made: (1) on the original borings, after thorough and prolonged mixing; (2) on the portion retained after 5 min. sieving, by a 300-mesh sieve; (3) by a 900-mesh sieve; (4) by a 4900-mesh sieve; (5) the fine powder that passed through the 4900-mesh sieve. Analyses of samples obtained by the ordinary method of sampling showed that the results are good when the content in graphite is not above 2%, but the results differ considerably from the calcd. figures when the graphite exceeds 2%. The % of graphite found is proportional to the fineness and increases with increase of amt. of graphite. Specimens A and B gave 0.84 and 3.74% graphite, resp., in series (1), 0.80 and 3.52 in series (2), while series (5) showed 1.18 and 7.84, resp. This is due to the simple mech. action that seps. the plates of graphite more easily from the coarser parts of the alloy. Total C increases while combined C decreases with increase of fineness. Si, up to the usual max. of 5% in cast irons, does not show such appreciable variations; it, however, shows a slight diminution in amt. with increase of fineness. P shows a considerable increase with increase of fineness, but the % of increase is proportionally greater for specimens contg. small amts. of P than for those contg. larger amts. Perhaps specimens contg. small amts. of P have the phosphides dissem-

inated in various states of combination as nodules or network throughout the mass of the alloy, while larger quantities of phosphides are distributed more uniformly; in the former condition the P follows the behavior of graphite as regards analytical results. As shows an appreciable increase with increase of fineness. S shows wide increases with increase of fineness, but the increase is relatively const. (about double). Mn shows in general a slight diminution, but on the other hand, when present with high S content, shows an increase with increasing fineness. This confirms the supposition that Mn and S are mutually combined. Where great precision is required in analysis of cast Fe, it is advisable to pulverize the whole of the borings or filings as finely as possible, to mix thoroughly, and then take a sample as usual.

ROBERT S. POSMONTIER

**Estimation of selenium.** LUIGI LOSANA. *Giorn. chim. ind. applicata* 4, 464-6 (1922).—The method for detg. Se is analogous to L.'s method for detg. S (*C. A.* 16, 2463). It consists in heating the substance contg. Se with Fe powder. The Fe selenide is then changed by successive treatment with HCl in a current of H to H<sub>2</sub>Se. This is detd. directly by absorbing it in a soln. of (AcO)<sub>2</sub>Zn and titrating iodometrically the selenide formed. By this method Se and S can be detd. separately, if both are present at the same time.

ROBERT S. POSMONTIER

**Determination of titanium in siderurgical products.** LUIGI LOSANA AND ENRICO CAROZZI. *Giorn. chim. ind. applicata* 4, 394-6 (1922).—The method is based upon the fact that methylene blue (*M*) oxidizes titanous compds. to titanic compds. in warm HCl soln. The reduction is not influenced by the presence of FeCl<sub>3</sub>, MnCl<sub>2</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, NH<sub>4</sub> molybdate and Na vanadate, either separately or in mixts. Use solns. of *M* contg. 3.90 and 1.95 g. per l., corresponding to about 0.001 and 0.0005 g. Ti per cc. The *M* solns. must be standardized frequently. The optimum temp. for the analysis is 40-60°. Use 2-5 g. of the sample to be analyzed. Treat with 1:1 HCl, take down gently to dryness, take up with HCl, and let stand for about 15 min. over a water bath at a low heat, to dissolve the Ti. Dil. to 200-300 cc., add 25 cc. HCl and a few g. Zn powder and allow to act for 30 min. at 60°. Make sure of complete reduction of the Fe. Filter rapidly through glass wool (having a few scraps of Zn upon the wool) into a flask full of CO<sub>2</sub> gas. Titrate at once with the *M* soln. to a persistent tint that increases decidedly with further addn. of 2 drops. The time required is very short. In the case of Fe-Ti alloys insol. in acids, break up 0.5 g. of the finely powdered sample with KHSO<sub>4</sub>, take up with 1:1 HCl, digest for 20 min. on the water bath, and without filtering off the SiO<sub>2</sub>, transfer to a graduated flask, bring to vol., take an aliquot part containing 0.1-0.2 g. substance, and proceed as above. R. S. P.

**Estimation of the methyl group in methylated thiolbenzenes.** J. POLLAK AND ANNA SPITZER. *Monatsh.* 43, 113-20 (1922).—The detn. of the MeS group by a method analogous to Zeisel's process for the MeO group is complicated by the fact that H<sub>2</sub>S and MeSH are evolved along with MeI during the decompn. by HI. The proposed process consists in the decompn. of the substance with HI (d. 1.7) and passing the vapors through a paste of red P and weakly acidified CdSO<sub>4</sub> soln. to remove I<sub>2</sub>S and thence into alc.-AgNO<sub>3</sub>. The ppt. is ignited and the mixt. of Ag and AgI completely converted into AgI for weighing.

C. J. WEST

**The assay of tin concentrates by the cyanide method.** A. F. S. ANDERSON. *Chem. Eng. Mining Rev.* 15, 119-20 (1922).—Methods developed in Brit. Malaya and W. Siam are outlined. The ore is ground to pass a 100-mesh sieve, acid treated, filtered, fused with KCN, the button weighed, hammered, rolled, cut and the fracture noted. *Acid treatment.*—(1) For ores with over 70% Sn or with Pb. Add to 10 g. ore 7 cc. H<sub>2</sub>O, 40 cc. concd. HCl for clean ores (60 cc. for dirty ores), 15 cc. HNO<sub>3</sub>, and warm 35-45 min. until the SnO<sub>2</sub> is a clean gray color. (2) For dirty ores or those contg. Ti. Add to 10 g. ore 7 g. H<sub>2</sub>O, and 15 cc. concd. H<sub>2</sub>SO<sub>4</sub>, warm 30 min., cool, add 30 cc. concd. HCl,

10 cc. concd.  $\text{HNO}_3$  and warm 30 min. Longer digestion is necessary with some dirty ores. If  $\text{WO}_3$  shows on the filter, wash with  $\text{NH}_4\text{OH}$  (1 : 1). *KCN fusion*.—Burn off in a crucible in a furnace the filter paper from 10 g. ore, add 40 g. KCN and 5 g. charcoal. Fuse 12–25 min., starting at a low heat and ending at  $1200^\circ$ . Numerous analyses gave a mean loss of 0.056 g. Sn per 10 g. ore in this fusion. The Sn buttons always contain impurities. The  $\text{H}_2\text{SO}_4$  method of cleaning gives cleaner buttons than the aqua regia. Clean concentrates give buttons contg. 0.2–0.3% impurities and those contg. Ti give over 0.3%. Since these are more than offset by the loss of Sn in fusion the method gives approx. results on the low side. C. C. DAVIS

The rapid estimation of chlorine in organic compounds. E. VOTOČEK. *Chem. Listy* 16, 248–9(1922).—V. combines the method of Marcusson and Döschner (*C. A.* 4, 2427) with his titration of chloride against a mercuric salt in the presence of Na nitroprusside as an indicator. The combustion is carried out in a funnel-shaped vessel of several l. capacity fitted with a stopcock. Since sufficient H is present in the mol. to convert all the Cl into HCl, the products of combustion are absorbed by water and titrated directly against  $\text{Hg}(\text{NO}_3)_2$ . The estn. takes about  $1\frac{1}{2}$  hrs. J. C. S.

Methods for the estimation of small amounts of starch in plant tissue. F. E. DENNY. *J. Assoc. Official Agr. Chem.* 6, 175–91(1922).—The official acid hydrolysis and a modified takadiastase method were found to be unsuitable for detg. starch in cantaloupe seeds where less than 2% is present in immature and less than 0.2% in samples from ripe melons. Three methods given in detail were devised based on dissolving the starch in concd.  $\text{CaCl}_2$  soln. followed by (1) pptg. the starch as starch-iodide under standard conditions, titrating the I in the ppt. and comparing with known starch similarly treated; (2) pptg. as in (1), purifying by successive repptn., liberating starch by  $\text{Na}_2\text{S}_2\text{O}_3$ , repptg. under standard conditions and titrating the residual I; and (3) pptg. the starch with I, hydrolyzing the starch with acid and estg. the dextrose by the Association's official method and that of Scales (*C. A.* 13, 1990). Method (1) is believed to be the most convenient to det. starch in 0.1% steps, while (3), using Scales procedure, although tedious, gave promise of being improved to give greater sensibility. Method (2) is intermediate in both respects. Results are given with suggestions as to improvement and applicability to other kinds of tissue. They are recommended at present only for tissues contg. small amts. of starch. H. A. LEPPER

NOYES, ARTHUR AMOS. *A Course of Instruction in the Qualitative Chemical Analysis of Inorganic Substances*. Revised ed. New York: McMillan. 190 pp. \$2.25.

SISCO, F. T. *Technical Analysis of Steel and Steel Works Materials*. New York: McGraw-Hill Co., Inc. 543 pp. \$5.

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

Influence of tenacity on the grinding hardness of certain minerals. P. J. HOLMQUIST. *Geol. För. Förh.* 44, 485–504(1922).—Trials were made of the abrasive action of carborundum of different degrees of fineness upon various minerals. With CSI powder of 2–5 $\mu$ , made to abrade apatite and fluorite, resp., for 3 min., the losses were in the ratio of 1.39 of apatite to 1 of fluorite. With CSI 40–50 $\mu$  abrading 1 min. the loss ratio was 1.07 : 1; 100–150 $\mu$ , 0.90 : 1. With magnetite, CSI 30–40 $\mu$  abraded 10 times as much from the faces (110), (111) and (001) as CSI 5 $\mu$ . CSI 25 $\mu$  abraded about 4 times as much from face (001) as CSI 5 $\mu$ . The loss of magnetite (111) by abrasion with CSI 35–40 $\mu$  was 6.86 times that of quartz (0001), while with CSI 5 $\mu$  the loss averaged 1.22 times. Rutile (001) compared with quartz (0001) showed a loss of 0.84 : 1 with

CSi 5-10 $\mu$ . By increasing the fineness of CSi 10-20, 30-40, 40-50, and 50-60 $\mu$  the ratio of loss of rutile to loss of quartz was 1.06, 1.12, 1.21, and 1.46 to 1, resp. Topaz (001) with CSi 2-5 $\mu$  lost on the av. 2.26 times as much as quartz (0001), while with topaz (.1 001) the loss averaged 1.06 : 1, but increased fineness of CSi raised the ratio of loss of topaz to loss of quartz to 1.50.

L. W. RIGGS

**Crystal structure of natural and of synthetic oxides of uranium, thorium and cerium.** V. M. GOLDSCHMIDT AND L. THOMASSEN. *Videnskapselskabet's Skrifter. I. Mat.-Naturf. Klasse* 1923, No. 2, 48 pp.—The minerals *pitchblende*, *bröggerite*, *cleveite* and *thorianite*, and the pure oxides  $UO_2$ ,  $UO_3$ ,  $U_2O_5$ ,  $ThO_2$  and  $CeO_2$  were studied. Debye-Scherrer diagrams were made by means of rays from a Hadding-Siegbahn metallic Röntgen tube with Al windows, the source of rays being an Fe anticathode. App., methods of work and of calcn. are described in detail. The results are shown in 18 tables. The crystal structures of *fluorite* and *ytrofluorite* were also examd. Detailed descriptions are given of the minerals and of the methods used in prepg. the oxides. Summary:  $UO_2$ ,  $ThO_2$  and  $CeO_2$  are isomorphous, the metallic atoms being arranged in face-centered cubic lattices. Three different geometrical possibilities exist for the arrangement of the O atoms, the most probable being that of the fluorite type. The cryst. structure of  $U_2O_5$  is essentially different from that of  $UO_2$ , and the crystals do not belong to the isometric system.  $UO_3$  was obtained only in the amorphous state. *Cleveite*, *bröggerite* and *thorianite* have a definite cryst. structure, with atomic arrangement corresponding to the original crystal lattice. The structure of these 3 minerals corresponds to that of isomorphous mixts. of  $UO_2$ ,  $ThO_2$  some  $CeO_2$  and eventually to the dioxide of U-Pb. Therefore *bröggerite* and the other varieties of uranium do not belong to the spinel group. The lattice dimensions ( $a \times 10^{-8}$  cm.) were:  $ThO_2$  5.61, *thorianite* 5.57, *bröggerite* 5.47, *cleveite* 5.47,  $UO_2$  5.47, and  $CeO_2$  5.41. *Cleveite*, which is rich in  $UO_3$ , is transformed to  $U_2O_5$  by heating to 800°. *Bröggerite* after heating has the structure of  $UO_3$ . *Pitchblende* from Joachimstal contains cryst. material of the isometric system in a strongly dispersed condition. The U atoms are arranged in face-centered cubes with edges 5.42-5.45 ( $10^{-8}$ ) cm., therefore smaller than those of pure  $UO_2$ , perhaps in consequence of isomorphic replacement of U by an atom of smaller vol. The cryst. structure of *ytrofluorites* is closely related with that of the fluorites, the edge of the elementary cube being 5.49 ( $10^{-8}$ ) cm. against 5.47 for fluorite. In *ytrofluorite* the F atom is not arranged as in fluorite. Probably the taking up of an excess of O in the crystn. of  $UO_2$  is in its geometrical relation comparable to the taking up of an excess of F atoms in *ytrofluorite*. It is noteworthy that minerals so strongly radioactive and so old as *bröggerite* and *thorianite* can entirely or largely keep their original atomic arrangement, notwithstanding for example in *bröggerite*, perhaps one out of 8 U atoms is transformed into Pb.

L. W. RIGGS

**The occurrence of element number 72 (hafnium) in malacon and alvite.** V. M. GOLDSCHMIDT AND L. THOMASSEN. *Norsk Geol. Tidsskr. Særtryk* 7, No. 1, 61-8 (1923).—From its position in the periodic table, it would be expected that the new element 72, hafnium, would occur in Zr and Th minerals. By use of a Roentgen-spectrographic apparatus the lines of hafnium were identified in malacon and alvite (varieties of zircon). Hafnium was found in appreciable amounts in alvite from Kragerø, which also contained Zr, Th, Fe, Mn, Yt, Th, Ce?, W?; its formula being  $(Zr, 72, Th)O_2 \cdot SiO_2$ . Malacon from Hitterø contained Zr, 72, Fe, Mn, Yt, and W. Such minerals are then possible sources of hafnium.

E. F. HOLDEN

**Iodargyrite from Montmins, near Echassières, Allier.** F. SCHNAEBELÉ. *Bull. soc. franc. mineral.* 45, 62-72(1922).—Iodargyrite crystals are associated with pyromorphite, mimetite, quartz, and fluorite. Several types of development are described, 12 forms being present and  $c = 0.8196$ .

E. F. H.

**Crystalline structure of silver iodide, marshite (CuI) and miersite (4AgI.CuI).** G. AMNORFF. *Geol. För. Förh.* **44**, 444-81 (1922).—Both the Laue and Debye methods were employed in this study. The results are shown in 7 tables and 5 diagrams. AgI at ordinary temp. gives Laue diagrams with hexagonal symmetry. From the indices-field the axial ratio of the type  $c : a \sim 1.6 : 1$  is obtained. By the Debye method 2 mols. of AgI are shown to be present in the elementary parallelepiped. Marshite and miersite both show regular structure of the sphalerite type. L. W. RIGGS

**Newly found iron meteorite from Somerset County, Pa.** G. P. MERRILL. *Am. J. Sci.* **5**, 175-6 (1923).—This 18-kg. meteorite was plowed up in 1922. In many respects it resembles the Mt. Joy, Adams Co., fall. By etching a large surface its octahedral nature was disclosed. Analysis by J. E. Whitfield gave: Fe 93.256, Ni 6.42, Co 0.325, P 0.037, Si 0.01, C 0.015, sum 100.063%, which differs from the Mt. Joy meteorite principally in the Ni, the latter contg. 4.81%. Following the usual custom this will be designated the New Baltimore Iron. L. W. RIGGS

**Platinum, gold, and silver in Colombia.** K. MIELEITNER. *Edel-Erden und Erze* **4**, 13-5 (1923).—The history of Au, Ag, and Pt mining in Colombia is described. Statistics of production, and notes on the locations of deposits are given. E. F. H.

**Carnotite in Southern Nevada.** D. F. HEWERT. *Eng. Mining J.-Press* **115**, 232-5 (1923).—One area near Sloan occurs in rhyolite. At Goodsprings and Sutor the deposits occur in Permian limestone and above it. Carnotite forms a thin canary-yellow coating on the joint walls, probably formed by downward percolating surface waters. The deposits are not of com. value. W. H. NEWHOUSE

**The nickeliferous pyrrhotite deposits of the Campello Mountains, Valle Strona, and of Miggiandone, Val de Toce.** B. LOTTI. *Rass. min. met. chim.* **57**, 105-7 (1922).—The deposits form a part of the eruptive basic rock composed of diorite, amphibolitic norite, granitiferous gabbro, peridotite and lherzolite extending from Ivrea to Locarno. At Miggiandone and in the Campello Mts. the deposits are chiefly Ni- and Co-bearing pyrrhotite. At Miggiandone these are associated with chalcopyrite, and elsewhere in the Toce valley with Fe and Cu sulfides. All deposits occur as lenticular, amygdaloid or spheroidal veins and masses in contact with gneiss, mica and calcareous schists and limestone. The Ni ores of the Campello Mts. are probably the richest known, contg. 7% Ni. C. C. DAVIS

**Magmatic autocatalysis and the protopneumatolytic minerals of igneous rocks.** F. LOEWINSON-LESSING. *Bull. soc. franc. mineral.* **45**, 34-47 (1922).—Primary minerals of igneous rocks may be classified as: (1) those which can crystallize from a dry fusion, and which have been artificially produced; (2) the *protopneumatolytic* minerals, which require the presence of mineralizers (OH, H<sub>2</sub>O, Cl, F, CO<sub>2</sub>, SO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>) for their formation. Plagioclases, pyroxene, olivine, nephelite are examples of class 1. The protopneumatolytic minerals are characteristically found in plutonic or intrusive rocks, many occur in alkaline rocks, nepheline syenites, or pegmatites, and associated with the rare earths. Many contain either F or Cl. While some of the minerals of that class may be usually considered secondary, at times they are certainly primary. The conditions of formation of the following are taken up: amphiboles, sodalite, scapolite, chlorite, epidote, zoisite, serpentine, analcite, orthoclase, quartz, micas, and garnets. E. F. H.

**The Illinois pyrite inventory of 1918.** G. H. CADY. Ill. State Geol. Survey, *Bull.* No. 38, 427-34 (1922).—The national S situation with reference to domestic and Canadian production of pyrite, production of S in La. and Tex., and the cutting off of imports of pyrite from Spain is reviewed. A rapid survey showed that the U. S. could easily make up any deficiency necessary to double the production of H<sub>2</sub>SO<sub>4</sub>, and that Ill. could produce 200,000 tons of pyrite annually without, or 500,000 tons with additional equipment. Several pyrite deposits are described. L. W. RIGGS

**Potash possibilities in Illinois.** C. R. SCHROYER. Ill. State Geol. Survey, *Bull.* No. 38, 435-40 (1922).—*Greensand* in Pulaski Co. carries 6.22% of  $K_2O$ . The extent of this greensand deposit is unknown. K as a by-product of the cement industry is briefly discussed. Analyses of 8 Ill. *shales* by Bleininger gave an av. of:  $SiO_2$  61.56,  $Al_2O_3$  16.12,  $Fe_2O_3$  2.96,  $FeO$  3.52,  $CaO$  0.94,  $MgO$  1.79,  $K_2O$  2.90,  $Na_2O$  0.82, ignition loss 6.72%. Other samples gave as high as 5.0% of  $K_2O$ . The ratios of  $SiO_2$  to  $Al_2O_3$  in 2 samples were 3.02 and 3.37, respectively, which is within the limits for cement material.

L. W. RIGGS

**Optical fluorite in southern Illinois.** J. E. POGUE. Ill. State Geol. Survey, *Bull.* No. 38, 419-25 (1922).—Previous to the war optical fluorite for use in America was imported through German dealers. Several deposits are described from which optical fluorite has been shipped. There appears to be sufficient optical fluorite in Ill. to supply the needs of the U. S. Suggestions for mining and shipping are given. L. W. R.

**Recent advances in science—geology.** G. W. TYRRELL. *Science Progress* 17, 361-8 (1923).—Includes a review of recent work on the chemistry of the igneous rocks.

J. S. HEPBURN

New oil fields of the Los Angeles Basin (LOHL) 22. An optical study of mixed crystals of ammonium and potassium Seignette salts (BACUVIER) 10. A crystallographic study of some complex compounds of iridium and rhodium (DUFFOUR) 6.

HUDSON, F. S.: *Geology of the Cuyamaca region of California with Special Reference to the Origin of Nickeliferous Pyrrhotite.* Berkeley, Calif.: Univ. of California, 252 pp. \$1.25.

## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

**Recent developments in metallurgy in Canada.** G. J. MACKAY. *Can. Mining J.* 44, 23-4 (1923).

A. BUTTS

**Manganese bronze; the use of scrap.** F. A. LIVERMORE. *Brass World* 19, 43-4 (1923).—Scrap contg. no As nor Sb will produce castings equal in quality to those from virgin metals.

W. H. BOYNTON

**Gold, silver, copper, lead and zinc in Idaho and Washington in 1921.** C. N. GERRY. U. S. Geol. Survey, *Mineral Resources of U. S., 1921*, Part I, 399-428 (preprint no. 25, published Feb. 12, 1923).

F. H.

**Gold, silver, copper, lead and zinc in Nevada in 1921.** V. C. HEIKES. U. S. Geol. Survey, *Mineral Resources of U. S., 1921*, Part I, 369-98 (preprint no. 24, published Feb. 10, 1923).

E. H.

**The nickel industry in 1921-1922.** A. J. WADHAM. *Ind. Eng. Chem.* 15, 409-10 (1923).

E. J. C.

**Direct smelting of wrought iron from ore by Basset's process.** I. MÓSCICKI. *Przemysł Chem.* 6, 73-81 (1922).—Wüst's objections (*C. A.* 16, 1381) are regarded as unfounded in view of the fact that he did not take the dissociation of  $CO_2$  into account in calcg. the temp. of combustion. The temp. of  $2560^\circ$  quoted by Wüst for open-hearth furnaces should be only  $2220^\circ$ , which is only  $25^\circ$  above the value calcd. for Basset's process. Further, with the rotary furnace a lower flame temp. than that required in the open-hearth furnace would suffice, and it may be accepted that combustion temps. quite sufficient for smelting iron can be developed in Basset's furnace. J. S. C. I.

**Sintering iron-bearing materials.** R. L. LLOYD. *Mining Met.* (Oct., 1922), 17-9.—Iron blast-furnace flue dust, owing to its C content, on sintering in a Dwight-



Lloyd furnace usually gives sinter of a very good quality, but if the C (coke) content is too high the sinter becomes very friable. The furnace works at its max. capacity and the product is strongest and most massive when the fines contain 8% of coke; dust contg. larger percentages should be mixed with pyrites cinders or fine ores to reduce the C to 8%. For the fine iron-ore concentrates from 8 to 3% of coke fine is sufficient according to whether the ore is magnetic or non-magnetic. The product in all cases is a coke-like mass of  $\text{Fe}_2\text{O}_4$ , which is exceedingly porous and eminently suitable for blast-furnace work, being very quickly and smoothly reduced by the gases; in addn. practically all the S in the ore is removed in the process. J. S. C. I.

**Calorific value of steel-making elements.** H. D. HIBBARD. *Iron Age* 111, 143-4, 211-3, 347-9(1923).—A discussion of the chemistry of fusion in the metallurgy of Fe. The calorific power of the various elements of importance in Fe and steel making is given. H treats individually the influence of each element on the metallurgy of Fe including O, C, Si, Al, Mg, P, Ti, Cr, S, V, Mn, Ni, As and Cu. H. C. PARISH

**Smelting silica bricks with reverberatory slags in a copper blast furnace.** R. F. WOOD. *Eng. Mining J.-Press* 115, 404-7(1923).—Unusual changes were sometimes necessary during the World War. As a result Cu-impregnated  $\text{SiO}_2$  brick and reverberatory slag, for instance, were both used. Either of these materials would be undesirable if used alone. It was found possible, however, by proper combinations to use them together. While there was a tendency toward formation of salamanders, even with unusual precautions, the practice was so developed as to get very satisfactory results, considering the unusual and difficult materials. W. discusses development of these changes in practice. H. C. PARISH

**Water in blister-copper bars and pigs.** A. R. LEDOUX. *Mining Met.* (Oct., 1922) 7-9.—The upper surface of pigs of blister Cu is generally very porous, and attention is drawn to the possibility of shipments that have been exposed to rain contg. considerable quantities of water which does not dry out after exposure to sun. In some shipments examd. the water content amounted to between 4 and 16 lb. per ton. The moisture content of a shipment is detd. by drying a selected no. of bars at 300-600° F. (150-315°), in a small gas- or oil-fired furnace. J. S. C. I.

**Notes on osmiridium.** J. R. THURLOW. *J. Chem. Met. Soc. S. Africa* 22, 209-10(1922).—Osmiridium occurs in the gold ores of the Eastern Rand (Transvaal) to the extent of 1 oz. to 5000-15,000 tons, and during treatment of the ores it accumulates in the "black sands," which consist chiefly of pyritic minerals with some ilmenite and chromite. These concentrates are treated on a batea to obtain a product contg. about 40% of osmiridium, which is further coned. to 90-95% by careful hand-panning. All the tailings are further treated on small canvas tables, and the concentrates are finally cleaned by treatment with acids. Analyses of a no. of concentrates and of a typical "black sand" are given. J. S. C. I.

**Powdered coal in the lead blast-furnace.** E. H. HAMILTON. *Mining Met.* (Oct., 1922) 25-7.—The working of a lead blast-furnace fired by means of powd. coal fed through the tuyères has been examd., and tables are given showing the heat distribution and output of metal and mat compared with the ordinary method of working. While the new process of firing slows down the output by about 6%, a greater recovery of metal is effected, together with a slight saving of fuel. J. S. C. I.

**Select sand for brasswork.** I. CHARLES VICKERS. *Foundry* 51, 152-4(1923).—The tendency now is to obtain venting more by the selection of a sand with open grain than by vent wires. If too little silt is present a smooth casting will not be obtained; if too much, blowing of the mold may occur. Silicates of Fe and Al are the principal bonding materials; they may vary from 5 to 17%. Sands high in  $\text{Fe}_2\text{O}_3$  and CaO can hold more moisture without becoming wet and make stronger molds. It is desirable to have a

clay binder with a high fusing temp. While Na and K silicates are not desirable for molds for high-melting mixts., they are not so objectionable for brass, bronze, etc.

H. C. PARISH

**A rare case of tellurium poisoning.** W. ADOLPHI. *Chem.-Ztg.* 46, 722(1922).—Three cases of acute poisoning by tellurous acid occurred during the smelting of some Pt mud which had been obtained as a by-product from Siberian Au ores contg. as impurities tellurides of Au and Ag. During the melting, the tellurous acid volatilized with the accompaniment of a white fume and a greenish flame. The symptoms observed in the victims were weakness, dizziness, greatly accelerated frequency of breathing and of the pulse, and a foul garlic-like odor of the breath. It lasted 8-10 weeks in one case.

J. S. C. I.

**Change of structure in silver above 500°.** M. KAHANOWICZ. *Atti accad. Lincei* 31, 313-5, 364-6(1922); *Science Abstracts* 25A, 785.—The results of expts. are given on the properties of Ag as the temp. is raised to 1227° K. The investigation includes measurements of emissive power, resistance-temp. coeff., and thermoelec. e. m. f. In each case it was found that the metal behaved normally up to a temp. of about 570°, but that above this point a marked modification in values took place, indicating a gradual change of internal structure. This change is demonstrated by photomicrographs, reproduced in the paper. At 800° the elements of a cellular structure begin to appear, and large crystals are found at 870°.

H. G.

**The influence of oxide in its various forms in the thermal treatment and fusion of copper.** LÉGRIS. *Rev. soudure autogène* 398-400 (Jan., Feb., Mar. 1922); *Rev. métal* 20 (Extraits), 1-5(1923).—On fusing sheet Cu contg.  $\text{Cu}_2\text{O}$ , the latter assumes the eutectic form. Under the influence of alternate mech. and thermal treatments, the  $\text{Cu}_2\text{O}$ , eutectic is reduced to isolated grains. No eutectic is formed in sheet Cu contg.  $\text{Cu}_2\text{O}$  which is brazed with brass or Ag. The "burning" of Cu by overheating during brazing or forging is due to the transformation of free  $\text{Cu}_2\text{O}$  into eutectic at a temp. but slightly lower than the m. p. of Cu, and not to exterior oxidation as previously thought. This "burning" is entirely eliminated if the Cu is free from  $\text{Cu}_2\text{O}$ . The presence of eutectic  $\text{Cu}_2\text{O}$  renders the Cu unfit to be worked mechanically. This explains the failures so frequently met with in oxy-acetylene, arc, or elec. welding of sheet Cu; the few successful and satisfactory results being due to an accidental freedom of the metal from  $\text{Cu}_2\text{O}$ , which was more frequent prior to the war than now. A deoxidizer is necessary to remove oxide in the fused metal; but it cannot remove the  $\text{Cu}_2\text{O}$  from neighboring points where the temp. is high enough for the formation of eutectic. This explains why breaks generally occur next to the weld; the deoxidizer has removed the oxide from the weld itself, but the high temp. has caused right beside the weld the formation of  $\text{Cu}_2\text{O}$  which cannot be removed. Welding can be successful only with perfectly deoxidized Cu. The Cu of unwelded tubes seems to have a different origin from that of sheet Cu. It contains grains of pseudo- $\text{Cu}_2\text{O}$ , which looks very much like normal  $\text{Cu}_2\text{O}$ , but which does not give the reactions, is not converted into eutectic on fusing, and does not present the same drawbacks in mech. working. LeG. suggests that these grains are due to deoxidation or to the addn. of some ingredient of which he does not know the compn. It is readily identified by heating to fusion the end of a small strip of the metal and examing micrographically. The presence of eutectoid indicates normal  $\text{Cu}_2\text{O}$  and its absence the presence of pseudo- $\text{Cu}_2\text{O}$ . Etching with  $\text{FeCl}_3$  in dil. HCl colors  $\text{Cu}_2\text{O}$  black, and etching with ammoniacal CuO shows up the eutectic. The eutectic can be completely destroyed by prolonged annealing; but this is not commercially practical. Numerous photomicrographs are given, including two which illustrate the manner in which welded pieces break beside the weld.

A. PAPINEAU-COUTURE

**Methods of handling materials in the electric furnace and the best type of furnace**

to use. (Heat treatment). F. W. BROOKS. *Trans. Am. Electrochem. Soc.* 43(Pre-print).—A general discussion, with designs, of various types of elec. furnaces, such as, the plain box, the special box, the car, the recuperative and continuous types. Advantages and disadvantages of each and methods of handling the material to insure uniform temp. and high efficiencies are outlined.

W. H. BOYNTON

Notes on several phenomena observed in the thermal treatment of tools. E. Y. LIPSKY. *Messageur direction gén. ind. métaux russe* No. 34, 50-8(Mar., Apr. 1922); *Rev. métal.* 20, (Extraits), 50-1(1923).

A. PAPINEAU-COUTURE

Choice of a magnetic steel. A. N. BOIKO. *Communic. trav. techn. sci. Rép. Russe* 5, 90(1921); *Rev. métal.* 20(Extraits), 106(1923).—The magnetic properties of steel are intimately related to the production of an alloy having a finely pulverized texture as is the case with martensite during the first moments of its formation. Steel contg. W 5-5.5% and C 0.6-0.8% is best suited for the manuf. of permanent magnets. Owing to the present shortage of W, steel contg. Cr 1.5-6% and C 0.6-0.8% can be used. Owing to the hardness of this steel, it should be annealed before being worked cold.

A. P.-C.

Influence of cold rolling on the properties of electrical sheet steel. Y. NIWA AND J. MINAMIZAWA. *Researches Electrotech. Lab. Japan* 117, 48 pp.(1922).—Two series of samples (Si steel and ordinary steel) are subjected to cold rolling from 0.46 mm. and 0.39 mm. To 0.08 mm. resp., and the elec., magnetic and mech. properties at every stage of rolling are measured. The rate of increase of hysteresis loss is nearly proportional to the reduction in thickness. Coercivity changes are similar to hysteresis changes, while the retentivity does not change appreciably during cold rolling. From  $B$ - $H$  curves at different reductions, the magnetizing force corresponding to 3,000  $B$ , 6,000  $B$  and 10,000  $B$ , the max. permeability, magnetic induction and magnetizing force corresponding to max. permeability, etc., are obtained. The magnetizing forces for 3,000  $B$  and 6,000  $B$  increase gradually with the reduction of thickness while that for 10,000  $B$  decreases near the final reduction. This is explained by the inhomogeneity of material. The initial max. permeabilities are different for both series while the final values are nearly equal. Also the magnetizing force for max. permeability increases with reduction, but the corresponding magnetic induction is nearly 4,000 gauss and does not change appreciably. The mech. properties are much affected during the initial stage of rolling, and are always accompanied by corresponding changes in magnetic properties. Cold rolling causes no marked change in the elec. resistivities and the d.

W. OGAWA

Physical and chemical properties of oil country tubular material. F. N. SPELLER. *Petroleum World* 20, 56-60(1923).—The properties of low-C steel for pipe line, tubing and casing are discussed.

D. F. BROWN

Rate of variation in the texture of alloys. A. N. BOIKO. *Communic. trav. techn. Rép. Russe* 5, 95(1921); *Rev. métal.* 20(Extraits), 74(1923).—From a discussion of the work of Guillaume, Laure, Braut, and of his own, B. concludes that the properties of all metals and all alloys change continuously. The variations can last tens, hundreds, and even thousands of years. The magnetic control of hardening and tempering has shown that in steel, at the ordinary temp., there is a decompn. of the solid soln. of austenite on the one hand, and a continuous growth of cryst. grains on the other. All the phys. properties of steel (linear dimensions, hardness, etc.) change as functions of this decompn. and this growth. Breaks and fissures which develop in steel constructions and objects are due to these changes. The law of mass action is applicable to these variations; this enables the changes to be expressed quantitatively by means of definite formulas, which are of the nature of exponential functions  $M = Ce^{-Kt}$ .

A. P.-C.

Studies on the aging of aluminium alloys. W. FRAENKEL AND E. SCHÜRER. *Z.*

*Metallkunde* 14, 49-58, 111-18(1922).—The effect of aging on the elec. and mech. properties of two Al alloys, *A* contg. 8% Zn and 0.5% Mg, and *B* contg. 4.5% Cu 0.5% Mg, and 0.5% Mn, has been studied. The resistance of the alloy gradually changes at a rate and to an extent depending on the temp. from which it has been quenched and the temp. of aging, *A* showing a max. alteration in the minimum time after quenching from 530° and *B* after quenching from 560°. In both cases the alteration of the resistance is smaller the higher the aging temp., although with higher temps. the change takes place more rapidly and at 100° occupies only a few minutes. The resistance of *A* to corrosion by HCl is very much increased by quenching from 530°, and still more so by aging the quenched alloy at ordinary temps. Aging at 100° increases the rate of soln. above that of the quenched alloy, while aging at 200° causes the alloy to dissolve twice as rapidly as it does in the annealed state. The e. m. f. of a cell contg. an annealed anode and an aged cathode of *A* is 0.1 v., while the freshly quenched alloy has a thermoelec. power (0-100°) of over 100 microvolts against the aged alloy. A noticeable decrease in density was also observed on aging *A*, but *B* showed a slight increase. Tests made on a series of similar alloys contg. increasing amts. of Mg showed that Mg up to 2% had very little effect on the tensile strength of either the annealed or quenched and aged alloys, but that it caused a considerable reduction of the sp. cond., the curve for the annealed alloys falling away concave to the axis of % Mg, while that for the quenched and aged alloys is convex to the same axis. A theoretical discussion of the changes taking place in the alloys during aging is given. J. S. C. I.

**Special aluminium bronzes. I. Copper-aluminium-nickel alloys.** LÉON GUILLET. *Rev. métal.* 20, 130-8(1923).—Four tables are given showing the compn. and mech. properties of 4 sets of alloys, the Cu content of each series (90, 83, 75 and 60%, resp.) being const. and the Al and Ni contents varying. The results are briefly commented on and 15 photomicrographs are given. The alloys fall into 2 classes: those with a low Ni content in which the Cu content is lower than in the binary Cu-Al alloy, and those having a high Ni content and 3% or less of Al. The properties of the latter are very remarkable, but their cost is high. A. PAPINEAU-COUTURE

**Iron aluminium alloys.** N. KOURNAKOV, G. OURASOV AND A. GRIGORIEV. *Ann. institut russe anal. physico-chimiques* 1, 11-33(1923); *Rev. métal.* 20(Extraits), 66-74 (1923).—After briefly reviewing previous work, the authors present the results of a detailed thermal, micrographic, and elec. investigation of Fe-Al alloys contg. 100-0% Fe. Curves are given for the thermal and elec. properties, and photomicrographs to show the structure. Conclusion: The alloys contain 3 constituents: Al, which constitutes the major portion of the Al-eutectic; phase  $\delta$  of variable compn.; and solid solns. of Al in  $\alpha$ - and  $\gamma$ -Fe. Phase  $\delta$  is independent and of variable compn. i. e., a "Berthollide." A. PAPINEAU-COUTURE

**Cutting and welding processes in foundries.** G. O. CARTEN. *Giesserei-Z.* 10, 39-42(1923).—The equipment and processes involving the use of O and C<sub>2</sub>H<sub>2</sub> are discussed. C. C. DAVIS

**Corrosion in condensers.** ERNEST BAYE. *Engineering World* 23, 16-8(1921); *J. Inst. Metals* 26, 534.—The causes of failure of tubes at 2 power stations in Sydney N. S. W. are described. At the first pitting caused failures in 2-3% of the tubes per yr. This was due to unsuitable compn. and to the American practice of prolonged annealing at 400°. At the second station there was little pitting, but end corrosion and dezincification occurred. The only serious pitting was in tinned brass tubes. *Exptl. tests.*—Hard-drawn Cu tubes failed by pitting at 80 times the rate of tinned brass tubes, and within 1 yr. 70% were removed. Dezincification with patent brass tubes was 100-200% worse than with Brit. Admiralty brass. Brass ferrules (60:40 compn.) were dezincified,

whereas Brit. Admiralty compd. was unaffected. With a 4-pass condenser the % of failures was approx. proportional to the square of the velocity of flow. An unusual fern-like Cu redeposition at tube-ends, ferrules, tube-plates and end-boxes was caused by a condenser standing in foul sea-H<sub>2</sub>O for 3 weeks. C. C. Davis

The basic-slag problem (JURRIZ) 15. The preservation of iron and steel by means of paint (FRIEND) 26. Rotary inclined horizontal drying drums (for ores) (U. S. pat. 1,447,929) 1. Oxidizable oil (U. S. pat. 1,447,954) 26,

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Obtaining intimate contact of liquids and gases in ore concentration. R. P. AKINS, F. D. GROSS and J. WM. BUCHER. Can. 228,862, Feb. 20, 1923. Definite quantities of liquid and gas are, resp., successively isolated and commingled and then released below the surface of a body of similar liquid. App. is specified.

Concentration of ore values. C. S. BRADLEY. Can. 228,784, Feb. 20, 1923. A cyclic process is specified for extg. metals of variable valency from ores, in which solns. contg. compds. of certain metals are used in the extn. and pptn. of other metals. Cf. C. A. 11, 1395.

Concentration of metals. C. S. BRADLEY. Can. 228,783, Feb. 20, 1923. Metals of variable valency are extd. from ores by subjecting them to the combined action of SO<sub>2</sub> and an aq. soln. of CaCl<sub>2</sub> in such excess as to maintain the resultant lower chloride of the values in soln.

Agglomerating fine ore and fuel in shaft furnaces. C. GIESECKE. U. S. 1,447,071, Feb. 27. A mixt. of fine ore and C is heated in the upper portion of a shaft furnace by reducing gas admitted just below the surface of the material, at a temp. too low to effect much sintering. After the ore has passed the combustion zone it is reoxidized by hot air rising through the furnace.

**Leaching ores or other materials.** J. A. BAKER. U. S. 1,447,637, Mar. 6. The material is fed continuously through a rotating horizontal leaching drum, from one end of the drum to the other, while the drum is kept more than half full of leaching liquid.

**Treating ore.** M. K. CODDING. Can. 228,660, Feb. 13, 1923. In recovering values from metallic ores by differential gravity sepn. or amalgamation, the ore is first violently agitated with a neutral electrolyte and an alk. electrolyte such as  $\text{NaNO}_3$  and  $\text{K}_2\text{CO}_3$ .

**Extracting metal compounds from ores.** J. S. WETZLAR. Brit. 188,865, Sept. 29, 1921. Ores are treated with  $\text{HNO}_3$  of at least 40% in the presence of Fe or acid-sol. Fe compds. equiv. to the metals other than Fe in the ore, the Fe nitrate produced being the effective attacking agent. After the sepn. of the Fe hydroxide, the nitrate soln. may be treated with  $\text{H}_2\text{SO}_4$  to ppt. the Pb and then by cementation to obtain first the Ag and the Cu; or the soln. after the removal of the Pb and Ag may be treated with  $\text{H}_2\text{SO}_4$  to obtain crystallizable sulfates, which, owing to their water of crystn., leave the liberated  $\text{HNO}_3$  in a concd. state. Alternatively instead of cementation as above described the metals may be obtained by fractional *electrolysis*.

**Extracting metals.** S. J. VERMAES and L. L. J. VAN LIJNDEN. Brit. 188,657, Nov. 6, 1922. Vapors of metallic chlorides are passed over a heated mixt. of C and alkalies, alk. earths, or  $\text{MgO}$ ; or the vapors of the chlorides mixed with excess of a gaseous or liquid reducing agent may be passed over the alk. substance alone. The temp. is kept sufficiently high to melt the metal and the chloride, which are both discharged in a molten state. The process may be carried out in a producer charged with carbonaceous fuel and burnt or unburnt limestone or dolomite, the chloride vapor being supplied thereto mixed with air.

**Metallic chlorides.** S. J. VERMAES and L. L. J. VAN LIJNDEN. Brit. 188,656, Nov. 16, 1922. O or roasted S ores are heated by direct, preferably oxidizing, heating to or above the temp. required for chloridizing, and then removed to another furnace, and mixed with chloridizing material such as  $\text{CaCl}_2$ . The second furnace is heated directly or by a limited amt. of gas within it, and a current of air or combustion gas is drawn through the furnace, preferably in countercurrent, so as to remove the volatilized chlorides without undue diln. The charge is agitated, for instance, by vigorous stirring, by fast rotation of the furnace, or by forcing or sucking air or gas through the ore. Both treatments may be effected in rotary furnaces, and the second furnace may be heated by burning gas in helical passages in the wall, part only of the furnace being thus heated, while in a part contiguous to the discharge end the cooling of the material by the countercurrent of air or gas is facilitated. In an example, the treatment of a Cu ore with  $\text{CaCl}_2$  is described, the temp. being  $820^\circ$ .

**Copper from ore concentrate.** C. S. BRADLEY. Can. 228,785, Feb. 20, 1923. The Cu content of ore is converted into  $\text{CuCl}_2 \cdot 3\text{CuO}$ , which is reduced with lime and C at a temp. below the m. p. of Cu and the reduced Cu is heated in a fused  $\text{CaCl}_2$  bath to fuse the Cu and free it from  $\text{CaCl}_2$ .

**Roasting sulfur-bearing ores.** M. F. CHASE, F. E. PIERCE and J. SKOGMARK. U. S. 1,447,645, Mar. 6. In roasting S-bearing ores of Zn, Fe, Cu or other metals, a gas mixt. consisting mainly of  $\text{SO}_2$ , N and O is circulated through a furnace in contact with the ore and O is introduced in sufficient amt. to produce a reactive medium of greater O content than air. A portion of the mixt. is withdrawn from circulation as required and a temp. control of the circulated gases is maintained.

**Apparatus of the Spitzkasten type for classifying and dewatering ores.** C. ALLEN. U. S. 1,447,610, Mar. 6.

**Apparatus for treating ores, etc.** C. J. REED. U. S. 1,447,888, Mar. 6. Solid material, e. g., Hg ore or ore to be desulfurized, is moved upward by a screw conveyor

through an inclined horizontal tubular chamber, the central portion of which is heated by burners placed beneath it, while a treating agent, *e. g.*, hot air or gas, is passed in the opposite direction through the chamber, *e. g.*, to volatilize Hg or S.

**Open-hearth furnaces.** F. B. MCKUNE. Can. 228,929, Feb. 20, 1923. Reissue Can. pat. 204,114, C. A. 14, 21, 3217.

**Consuming the poisonous gases in blast furnaces.** J. VORGELE. U. S. 1,447,581, Mar. 6.  $C_2H_2$  or  $C_4H_2$  and H are fed to burners near the top of a blast furnace in order to consume poisonous gases.

**Combustion furnace adapted for heating metal sheets or bars.** T. J. COSTELLO. U. S. 1,447,588, Mar. 6.

**Refining lead.** H. HARRIS. Brit. 189,013, Jan. 18, 1922. Oxidizable impurities, such as As, Sb, Sn, and Zn, are removed from Pb by bringing the molten Pb into contact with an oxidizing agent, such as alkali nitrate, nitrite, chlorate, or hypochlorite, or a peroxide, in suspension or soln. in molten caustic alkali, or caustic alkali and a fusible chloride. The molten metal is preferably passed through the reagent by means of the app. described in 142,398 (C. A. 14, 2613) or 184,639. The temp. and the proportion of oxidizing agent may be so adjusted that different impurities are removed in succession.

**High-speed steel.** KEITOKU KAMISHIMA. Japan. 40,316, Oct. 18, 1921. In a suitable elec. furnace Co and Mo are melted, V,  $CaF_2$  and straw ash are added and the temp. is maintained at 2,200–2,300°. In another furnace, Fe, W and Cr are heated to complete fusion. The first mixt. is added to the second and then the whole is poured into a mold. The product is a steel contg. above 18% W, above 4% Co, above 4% V, and above 2.5% Mo.

**Alloys.** ALUMINUM CO. OF AMERICA. Brit. 188,699, June 13, 1921. Al alloys contg. Cu and Mg, with or without Mn, Cr, or other metal, are improved by the addn. of an alkali metal. *E. g.*, up to 2% of Ca may be added to an Al alloy contg. about 4% of Cu and about 0.5% of Mg, with or without about 1% of Mn. The alloys may be made by utilizing suitable proportions of previously prepd. rich alloys of Al with the other constituent metals.

**Pickling iron or iron alloys.** BRITISH & FOREIGN CHEMICAL PRODUCERS, LTD. Brit. 188,713, July 12, 1921. To avoid brittleness in pickled Fe or Fe alloys, org. bases contg. N rings, especially the quinoline nucleus, are added to any usual pickling bath, which may comprise  $H_2SO_4$  of 5% strength for hot pickling, or HCl of 10–20% strength for cold pickling, and 1–2% of the N compd. Exts. from the distn. products of coal tar or fractions of coal-tar distillates which contain the bases, or synthetic products may be used. Cf. 158,768 (C. A. 15, 1878).

**Magnetic materials.** WESTERN ELECTRIC CO., LTD. Brit. 188,688, May 17, 1921. A magnetic material having high permeability at low magnetizing forces, of the order of 0.2 gauss or less, comprises Ni and Fe, *e. g.*, Ni 78.5% and Fe 21.5%. The material is particularly applicable for loading signalling conductors for use in connection with telegraphy and telephony, and also for relay armatures, frequency changers and modulators, transformer cores, and loading and choking coils. Cf. 189,075.

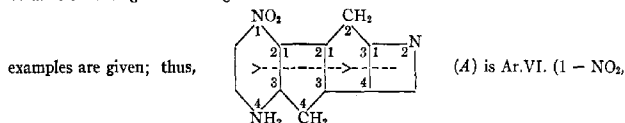
**Annealing.** J. HARTMANN. Brit. 188,343, Nov. 6, 1922. To prevent oxidation of the surface of metals undergoing annealing, a non-oxidizing non-combustible protecting gas is introduced into the annealing box during the cooling operation to prevent the entry of air. A suitable construction is specified.

**Casting piston ring blanks or similar articles.** J. M. PERRY. U. S. 1,447,817, Mar. 6. Bubbles or holes are avoided in casting by moving a ring through the molten metal in the mold to cause the gas bubbles to travel to a waste zone before the metal solidifies.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROULLER AND CLARENCE J. WEST

A new system for the linear representation of the structure of all organic compounds. T. SHERLOCK WHEELER. *Chem. News* 126, 33-5, 49-50, 66-7(1923).—A linear series of letters and figures is proposed, to replace the usual structural formula for concise use. It describes the mol., following an imaginary "structure line" from ring to ring and along chains. The prefixes Ar and Al denote aromatic and alicyclic structure resp., each symbol holding till canceled by the other. VI = 6-membered ring,  $\overline{\text{VI}}$  = 6-membered chain, and so for other Roman nos. Arabic nos. denote positions. Each ring is numbered independently and clockwise, beginning at the left of where the structure line enters. If the structure line must be branched, indices must be used to distinguish the rings or chains from which the branches start. Numerous



4-NH<sub>2</sub>)2,3V.(4=H<sub>2</sub>)2,3V.(2=H<sub>2</sub>)3,4IV.(N-2); CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CP<sub>r</sub>:CHCH<sub>2</sub>CH:CH<sub>2</sub> is  $\overline{\text{IX}}$ .(Δ<sup>6,8</sup>) 5(I $\overline{\text{V}}$ ). Centric bonds, stereoisomerism, etc. can be represented. The linear formula of a compd. may often be written in several different ways; naturally, the shortest one is preferred.

AUSTIN M. PATTERSON

A method for the naming of all organic compounds. T. SHERLOCK WHEELER. *Chem. News* 126, 113-5(1923).—W.'s linear formulas (cf. preceding abstr.) are translated into names, in which the Greek forms tetr-, pent-, etc. replace Roman nos. and -ar, -al, -an, -en and -in denote resp. aromatic ring, alicyclic ring, chain, double bond and triple bond. The Latin bi-, tri-, etc. are also used, e. g., to denote no. of substituting groups. Thus, A (above) is "hexar-(1-nitro, 4-amino)-2,3-pentar(4-bi-hydro)-2,3-pentar-(2-bi-hydro)-3,4-tetrar-(nitrogen-2)." W.'s system of org. class names (*C. A.* 15, 1693) can easily be fitted into the present scheme.

AUSTIN M. PATTERSON

The importance and application of ozone in organic chemistry. CURT RÄTH. *Z. angew. Chem.* 35, 717-9(1922).—The addn. of O<sub>3</sub> to unsatd. org. compds. is discussed, with numerous examples and literature references.

T. S. CARSWELL

Abnormal transformations of derivatives of isoprene and of β,γ-dimethylbutadiene. L. CLAISEN, F. KREMERS, F. ROTH AND E. TIETZE. *J. prakt. Chem.* 105, 65-92(1922).—*Derivs. of isoprene* (A).—Me<sub>2</sub>C:CHCH<sub>2</sub>Br (B) prepd. by the method of Mokijewsky (*Jahresber.* 1900, 560) had d<sub>4</sub><sup>15</sup> 1.2930 and b<sub>61</sub> 62-4°, leaving a residue of Me<sub>2</sub>CBrCH<sub>2</sub>:CH<sub>2</sub>Br(C). Catalytic hydrogenation in Me<sub>2</sub>CO by PdCl<sub>2</sub> to iso-AmBr was unsuccessful. By treating A with less HBr and distg. over NaOH *in vacuo* a product was obtained which could be sepd. into fractions of different b. p. By long boiling under 165 mm. the combined fractions increased their b. p. slowly from 75° to a const. 86°. It is inferred that the tert. bromide is first formed and is then transformed to the primary. B shaken with aq. Na<sub>2</sub>CO<sub>3</sub>, extd. with Et<sub>2</sub>O and dried over K<sub>2</sub>CO<sub>3</sub> and BaO, gave Me<sub>2</sub>C(OH)CH:CH<sub>2</sub> (D) (cf. *Jahresber.* 1900, 561). Treated with HBr, D reverted to B. B treated with alc. NaOHt gave the compound Me<sub>2</sub>C:CHCH<sub>2</sub>OEt, pleasant smelling liquid, b. 124.7-125°, d<sub>4</sub><sup>15</sup> 0.8005, decolorized by Br, not attacked by Na. B treated with PhMgBr gave PhCH<sub>2</sub>CH:CHMe<sub>2</sub> (E) (references to previous prepn. given), b<sub>74</sub> 204.5-207°, d<sub>4</sub><sup>15</sup> 0.8958. E heated with HBr in HOAc under pressure and distd. *in vacuo* gave the compound PhCH<sub>2</sub>CH<sub>2</sub>CBrMe<sub>2</sub>, thick liquid, b<sub>44</sub> 126-8°, with the odor of lemons, reverts to E by heating with quinoline, decompd. by H<sub>2</sub>O. A general method,



still unpublished, was developed for prepg. propenyl derivs. from aromatic allyl derivs. by boiling the latter with potash lime. By this method, *E* was transformed to  $\text{PhCH}=\text{CHCHMe}_2$ . *E* reduced in EtOH by H with  $\text{PdCl}_2$  formed  $\text{PhCH}_2\text{CH}_2\text{CHMe}_2$ . Attempts to obtain this from  $\text{Me}_2\text{CHCH}_2\text{CH}_2\text{I}$  and  $\text{PhMgBr}$  failed.  $\text{HCONHPh}$  boiled in  $\text{C}_6\text{H}_6$  with Na and *B*, dild. with  $\text{H}_2\text{O}$ , the  $\text{C}_6\text{H}_6$  layer dild. with benzine, the free  $\text{HCONHPh}$  removed with dil.  $\text{NaOH}$ , washed with dil.  $\text{HCO}_2\text{H}$ , dried, and distd. *in vacuo*, gave the compound  $\text{HCONPhCH}_2\text{CH}:\text{CMe}_2$  (*F*), thick oil,  $b_{16.4}$  163–4°,  $d_{16}^{15}$  1.029, *m.* below –20°. *F* warmed with  $\text{KOH}$  in abs.  $\text{MeOH}$  gave the compound  $\text{PhNHCH}_2\text{CH}:\text{CMe}_2$ ,  $b_{16.5}$  136–7°,  $d_{16}^{15}$  0.9583, with the odor of spearmint. *F* warmed with  $\text{C}_6\text{H}_5\text{N}$  and  $\text{BzCl}$  gave the compound  $\text{PhNBzCH}_2\text{CH}:\text{CMe}_2$  (*G*), stout, star-clustered prisms from hot  $\text{C}_6\text{H}_5$ -benzine, *m.* 80–1°, decolorizes Br in  $\text{CHCl}_3$  instantly. *G* reduced by H with  $\text{PdCl}_2$  formed the compound  $\text{PhNBzCH}_2\text{CH}_2\text{CHMe}_2$ , long, stout prisms from hot benzine, *m.* 75°. *Derivs. of  $\beta,\gamma$ -dimethylbutadiene (H).*—Procedures analogous to those described for *A* derivs. were used. Only 1 hydrogenation was effected because of the greater stability of isohexenyl, compared with isopentenyl, towards H. *H* and  $\text{HBr}$  at a low temp. gave the compound  $\text{Me}_3\text{CH}:\text{CMe}_2\text{CH}_2\text{Br}$  (*I*),  $b_{20}$  51–4°,  $b_{11}$  62–5°, *b.* 144–8° (decompn.),  $d_{16}^{15}$  1.254, a lachrymatory liquid of penetrating odor, turns brown on standing, decomps. in  $\text{H}_2\text{O}$  and in warm  $\text{HOAc}$ . With Br, *I* forms a dibromide, oil, decomps. slowly at room temp. and completely on distn. *in vacuo* to form the compound  $\text{C}_6\text{H}_{10}\text{Br}_2$ ,  $b_{11}$  115–9°. Like the formation of a tert. bromide from *A*, *H* treated with less  $\text{HBr}$  than in the prepn. of *I* gave a product with a wide range of *b. p.*, which on long boiling increased its *b. p.* to 50–4° under 20 mm. *H* treated with  $\text{HBr}$  at 0° for a long time and pptd. with petr. ether gave the compound  $\text{Me}_3\text{CBr}:\text{CHMeCH}_2\text{Br}$ , crystals with the odor of camphor, sublims 160–80°, decompd. by  $\text{HOAc}$ , can be titrated with dil. alc.  $\text{KOH}$ . *I* shaken with aq.  $\text{Na}_2\text{CO}_3$  gave  $\text{Me}_2\text{C}(\text{OH})\text{CMe}:\text{CH}_2$  (*J*) (cf. *Ber.* 22, 760(1889); *Bull. soc. chim.* 35, 978(1906)),  $d_{16}^{15}$  0.8527. Warmed with  $\text{BzCl}$  and  $\text{C}_6\text{H}_5\text{N}$  *J* formed the compound  $\text{H}_2\text{C}:\text{CMeC}(\text{OBz})\text{Me}_2$ , thick oil,  $b_{11}$  126–7°, decompd. by boiling at ordinary pressure. *J* and alc.  $\text{NaOEt}$  formed the compound  $\text{Me}_2\text{C}:\text{CMeCH}_2\text{OEt}$ ,  $b_{187}$  143–143.2°,  $d_{16}^{15}$  0.8167, with pleasant odor. *I* and  $\text{PhMgBr}$  formed the compound  $\text{PhCH}_2\text{CMe}:\text{CMe}_2$  (*K*),  $b_{150}$  220–1°,  $d_{16}^{15}$  0.9003, with an odor of geraniums, reduces  $\text{Hg}(\text{OAc})_2$  to  $\text{HgOAc}$ . *K* heated a long time in  $\text{HOAc}$  and  $\text{HBr}$  gave the hydrobromide,  $\text{PhC}_6\text{H}_5\text{Br}$ ,  $b_{18}$  134–6°, with the odor of orange peel, decompd. by quinoline and slowly by  $\text{H}_2\text{O}$  to *K*. *K* reduced by H formed the compound  $\text{PhCH}_2\text{CHMeCHMe}_2$ ,  $b_{188}$  216.5–7.5°,  $d_{16}^{15}$  0.8765, with an aromatic odor. Analogous to the formation of *F*, the compound  $\text{HCONPhCH}_2\text{CMe}:\text{CMe}_2$  (*L*) was obtained, thick oil,  $b_{18}$  169–71°, *m.* –20°, insol. in dil. acids and alkalis. Warmed with  $\text{KOH}$  in  $\text{MeOH}$ , *L* gave the compound  $\text{PhNHCH}_2\text{CMe}:\text{CMe}_2$  (*M*),  $b_{16.5}$  144–6°,  $d_{16}^{15}$  0.9622, turns orange in the air. *M* warmed with  $\text{BzCl}$  and  $\text{C}_6\text{H}_5\text{N}$  formed the benzoyl derivative,  $\text{C}_{19}\text{H}_{17}\text{NO}$ , thick, tetragonal plates from petr. ether, *m.* 97.5–8.5°. *I* in ice-cold benzene treated with  $\text{PhNH}_2$  in  $\text{Et}_2\text{O}$ , let stand several days, cooled, filtered and evapd., gave *di-isohexenylaniline*  $\text{PhN}(\text{C}_6\text{H}_{11})_2$ , prisms in roset form from  $\text{MeOH}$ , *m.* 58–9°, with properties of a weak base, sol. in warm dil.  $\text{H}_2\text{SO}_4$ . C. C. D.

Recent development in the chemistry of organic mercury compounds. F. C. WHITMORE. *Ind. Eng. Chem.* 15, 417–9(1923).—A bibliography of 37 titles accompanies this review. E. J. C.

The production of methanol from formaldehyde by "fermentation." H. MÜLLER. *Helvetica Chim. Acta* 5, 627–8(1922).—E. Müller (*C. A.* 16, 1078) found that by catalysis with Os  $\text{HCHO}$  and  $\text{H}_2\text{O}$  react to form  $\text{MeOH}$  and  $\text{CO}_2$ . He assumes the formation of a "dioxaldehyde,"  $\text{H}_2\text{CO}_2$ , contg. a hexavalent carbon atom, which breaks down to H and  $\text{CO}_2$ . According to Cannizzaro's reaction at ordinary temp.  $\text{HCHO}$  forms  $\text{MeOH}$  and  $\text{HCO}_2\text{H}$ . The latter under proper conditions may break down to  $\text{H}_2\text{CO}_2$ .

and HCHO. Os in this case induces an org. reaction which duplicates the processes of a true fermentation. This reaction shows the close relation existing between the so-called induced reactions, oxidation-reductions and true oxidations. C. N. FREY

**Estimation of acetone in methyl alcohol and the purification of methyl alcohol by sodium hypoiodite.** H. H. BATES, J. M. MULLALLY AND HAROLD HARTLEY. *J. Chem. Soc.* 123, 401-4 (1923).—NaIO and MeOH react to form some CHI<sub>3</sub> and probably other products, the incompleteness of the reaction between them being due to the rapid autoxidation of the former to NaIO<sub>3</sub>. This is of importance in the detn. of AcMe according to Messinger and the following standard conditions were used: 20 cc. MeOH were dild. to 100 cc. with H<sub>2</sub>O. 25 cc. of this soln. mixed with 20 cc. 0.5 N NaOH and 25 cc. 0.1 N I, the mixt. shaken at intervals for 0.5 hr., acidified with 0.5 N H<sub>2</sub>SO<sub>4</sub> and titrated with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. The temp. is maintained at 15° ± 0.5°. The zero error of the detn. is 0.5 cc. I, or 0.012% AcMe must be subtracted from the AcMe found. In purifying MeOH contg. 0.2% AcMe, 25 g. I are dissolved in 1 l. of the MeOH and the soln. poured with shaking into 500 cc. N NaOH. After standing overnight (adding H<sub>2</sub>O to ppt. the CHI<sub>3</sub> if necessary), the soln. is filtered, boiled to hydrolyze the CHI<sub>3</sub> in soln. and distd. The 1st fractionation gave 800 cc. 97% and 150 cc. 85% AcMe-free MeOH.

C. J. WEST

**An attempt to resolve quaternary phosphonium compounds.** L. G. RADCLIFFE AND W. H. BRINDLEY. *Chemistry Ind.* 42, 64-6 (1923).—*p*-Tolylphosphine dichloride (A) was obtained by heating a mixt. of PhMe and PCl<sub>3</sub> in the presence of AlCl<sub>3</sub> (*Ann.* 212, 303 (1882)). A was then converted to *p*-tolylphenylchlorophosphine (B) by heating with Ph<sub>2</sub>Hg (cf. *Ann.* 315, 59 (1901)). From B *p*-tolylphenylmethylphosphine (C) was prepd. by reaction with 4 mols. of MgMeI. The *p*-tolylphenylmethylallylphosphonium iodide (D), m. 175° (decompn.), was obtained by mixing C with C<sub>3</sub>H<sub>7</sub>I in Et<sub>2</sub>O. D was treated with an equiv. quantity of the Ag salt of *d*-bromocamphorsulfonic acid in dil. alc. soln.; the pptd. AgI was filtered off, and the filtrate evapd. to low bulk, when a jelly-like mass formed after long standing, but no crystn. took place. Upon warming a mixt. of D and BuI in Et<sub>2</sub>O, an oily ppt. was obtained, but no crystals. T. S. CARSWELL

**The amphoteric nature of the carbonyl group.** ERICH MÜLLER. *Z. angew. Chem.* 35, 689-92; 698-700 (1922).—A great no. of individual cases of oxidation and reduction of aldehydes and ketones, which cannot be adequately summarized, are described to show that the reaction rate can best be explained on an elec. dissociation basis as already developed for other compds. (cf. *C. A.* 15, 1501; 16, 1078, 3801). C. C. D.

**Mercuric derivatives of hexamethylenetetramine.** R. DOURIS AND G. BEYTOUR. *Compt. rend.* 176, 107-9 (1923).—New derivs. of Hg<sup>++</sup> salts and (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> are described. Aq. (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> and HgSO<sub>4</sub> acidified with H<sub>2</sub>SO<sub>4</sub> gave the compound (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>.HgSO<sub>4</sub>·H<sub>2</sub>O, fine needles, loses H<sub>2</sub>O above 100°, m. 177°, slightly sol. in H<sub>2</sub>O, decompd. by boiling H<sub>2</sub>O. Hot aq. Hg(CN)<sub>2</sub> and very concd. (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> gave the compound (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>·2Hg(CN)<sub>2</sub>, decomp. without melting 208-16°. The Hg could be detected by H<sub>2</sub>S, but not by NH<sub>4</sub>OH nor by KI. Cold satd. solns. of Hg(OAc)<sub>2</sub> and (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> gave the compound (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>.Hg(OAc)<sub>2</sub>, crystals, decomp. approx. 120°. The Hg could be detected by H<sub>2</sub>S and by (NH<sub>4</sub>)<sub>2</sub>S but not by NH<sub>4</sub>OH. The role of (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub> in these compds. is analogous to that in uroformine diphenate (cf. Bouchéreau, *Thèse Doct. Pharm. Paris* 1917, 22). The corrosive action of the Hg salt is reduced and the antisyphilitic action increased. Intravenous injection of (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>·2Hg(CN)<sub>2</sub> does not cause disturbances characteristic of Hg(CN)<sub>2</sub>. Also in *Repert. pharm.* 35, 79-81; *Bull. soc. chim.* 33, 311-3 (1923).

C. C. DAVIS

**Autöxidation. II. Antioxygenic power and related phenomena.** C. MOUREAU AND C. DUPRAISSÉ. *Compt. rend.* 175, 127-32 (1922); cf. *C. A.* 16, 1439.—Certain compds. (called antioxygens) inhibit the oxidation of many substances. Phenols

in particular possess this property. The oxidation of acrolein by itself and in the presence of hydroquinone was studied. Acrolein,  $O_2$ , and varying minute amts. of the antioxygen were enclosed over Hg in a series of barometer tubes. The oxidation was measured by the change in height of the column. The series was compared with a tube contg. pure acrolein. The suppression of oxidation was proportional to the amt. of antioxygen present. The method is claimed to be very accurate. Several other polyphenols possess this property. A short bibliography is given. JAMES A. BRADLEY

**The chromic oxidation of the homologs of acetic acid.** I. J. SIMON. *Compt. rend.* 175, 187-9(1922).—HOAc is not completely oxidized by a mixt. of  $CrO_3$  and  $H_2SO_4$  but is completely oxidized to  $CO_2$  if the  $CrO_3$  is replaced by  $Ag_2CrO_4$ . A table is given showing the % of the C content of the homologs that is oxidized by  $CrO_3$  and by  $Ag_2CrO_4$ . In every case the  $Ag_2CrO_4$  oxidizes practically all of the C, while the  $CrO_3$  oxidizes an amt. varying with the acid but always leaving unattacked an amt. corresponding to 1 or 2 atoms. The end-point of the oxidation is assumed to be HOAc. The following mechanism is suggested for the oxidation of the homologs of HOAc:  $RCH_2CO_2H \rightarrow RCOCO_2H \rightarrow RCO_2H$ . JAMES A. BRADLEY

**The spontaneous decomposition of cyanoacetyl chloride.** G. SCHROETER AND CHR. SEIDLER. *J. prakt. Chem.* 105, 165-76(1922).— $CH_2(CN)COCl$  (A) held at  $0^\circ$  with exclusion of  $H_2O$  liberated HCl and left a viscous, brown-yellow resin which, extd. with hot  $H_2O$  and evapd., gave yellow crystals and a yellow-brown, viscous,  $H_2O$ -sol.,  $Et_2O$ -sol. oil. The crystals were 2,4-dihydroxy-6-chloronicotinic nitrile (B), fine needles from  $H_2O$ , turns yellow-brown at  $187-90^\circ$ , decomp. without m., sol. in  $H_2O$  (1:100 at  $20^\circ$ , 1:9 at  $100^\circ$ ), hot EtOH,  $Me_2CO$ , HOAc and alkalies, sparingly sol. in EtOAc,  $Et_2O$  and  $C_6H_6$ , gives a deep red color in EtOH with  $FeCl_3$ , gives on cooling from hot NaOH the disodium salt,  $C_6HON_2ClNa_2 \cdot 6H_2O$ , compact crystals. Heated under pressure with aq. NaOH, B gave a Na compd. which was not identified, and either 2,4,6-trihydroxypyridine or 2,4,6-trihydroxynicotinic acid. B, heated at  $100^\circ$  with concd.  $H_2SO_4$ , let stand and dild. with  $H_2O$ , gave 2,4-dihydroxy-6-chloronicotinamide, sol. in alkalies but decompd. by long boiling, difficultly sol. in  $H_2O$ , HOAc and EtOH, decomp.  $220^\circ$ , gives in EtOH a deep red color with  $FeCl_3$ , gives on cooling from hot NaOH the disodium salt. B treated in aq. NaOH with  $Me_2SO_4$ , made alk. with excess NaOH and acidified with HCl, gave 2-hydroxy-4-methoxy-6-chloronicotinic nitrile, crystals from  $HCO_2H$ , decomp.  $250^\circ$ , difficultly sol. in  $H_2O$  and EtOH, gives in EtOH with  $FeCl_3$  a color less red than B, titrates in EtOH as a monobasic acid. It gave with Na in EtOH a monosodium salt (C), cryst. powder. C boiled with  $Me_2SO_4$  in xylene, filtered, and washed with dil. NaOH and  $H_2O$ , gave 2,4-dimethoxy-6-chloronicotinic nitrile (D), crystals from HOAc, m.  $239-40^\circ$  (decompn.), insol. in aq. NaOH (decompd. by boiling), gives no color with  $FeCl_3$ . D boiled with K in EtOH, and dild. with  $H_2O$ , gave 2,4,6-trimethoxynicotinic nitrile, crystals from HOAc, m.  $260-1^\circ$  (decompn.), sol. in concd.  $H_2SO_4$ , insol. in alkalies, gives no color with  $FeCl_3$ . C. C. DAVIS

**The Sandmeyer synthesis of chloroiminocarbonic esters and formhydroximic esters as a preliminary step in the formation of cyanic esters.** J. HUBEN. *J. prakt. Chem.* 105, 7-26(1922).—As reagents for prep. the hitherto unknown cyanic esters, ROCN, several formhydroximic acid esters not previously known were prepd. The Sandmeyer method (cf. *Ber.* 19, 882(1886)) for the prep. of  $(EtO)_2C:NCl$  (A) was used in modified form. By replacing the KCN by KOCN, no A was formed, but  $ClCH_2CH(NHCO_2Et)_2$  (C) (cf. *Ber.* 7, 628(1874); *J. prakt. Chem.* 24, 120(1881)). C was also prepd. by warming B with  $EtOCHClCH_2Cl$  (D). An attempt to prep. C from Cl and aq. B gave the compound  $Cl_2NCO_2Et$  (E), an explosive heavy golden oil,  $b_p$   $66-7^\circ$ , with intense penetrating odor, darkens and burns the skin, volatile with steam, sol. in EtOH,  $Et_2O$  and warm  $NH_4Cl$  soln. With  $KNO_2$  soln. a green color with brown

fumes appeared, with violent decompn. With KI soln. I sepd. *E* shaken with *B* and EtOH or with *B* and HCl and let stand gave  $\beta$ -chloroethylideneurethan, cryst. mass. Ice-cold aq.  $\text{H}_2\text{NCO}_2\text{Me}$  (*F*) treated with Cl gave the compound  $\text{Cl}_2\text{NCO}_2\text{Me}$ ,  $b_{11}$  56–7°, similar in phys. and chem. properties to *E*. *D* heated with *F* gave the compound  $\text{ClCH}_2\text{CH}(\text{NHCO}_2\text{Me})_2$ , crystals from  $\text{H}_2\text{O}$ , m. 136°, sol. in EtOH and  $\text{Et}_2\text{O}$ . Reduction of *A* (cf. C. A. 7, 3502) to  $(\text{Et}_2\text{O})_2\text{C}:\text{NH}$  (*G*), the latter shaken in EtOH with  $\text{PhNH}_2\text{Cl}$ , warmed, let stand, evapd., washed with EtOH, filtered, the EtOH evapd. *in vacuo*, the  $\text{CO}(\text{NHPh})_2$  filtered and the filtrate fractionated, gave the compound  $\text{PhN}:\text{C}(\text{OEt})_2$  oil,  $b_{16}$  136–7°, with an odor like  $\text{PhNH}_2$ , decompd. by mineral acids. In prepg.  $\text{NH}_2\text{OH}$  by the method of Lecher and Hofmann (cf. C. A. 16, 3598) addn. of  $\text{Et}_2\text{O}$  to the alc. soln. sepd. from NaCl increased the yield.  $\text{NH}_2\text{OH}$  in cold  $\text{Et}_2\text{O}$  treated with  $\text{HN}:\text{CH}(\text{OEt})$ ,  $\text{K}_2\text{CO}_3$  added, the  $\text{Et}_2\text{O}$  layer dried over  $\text{Na}_2\text{SO}_4$  and evapd. *in vacuo* gave the compound  $\text{HON}:\text{CH}(\text{OEt})$  (*H*), long needles from  $\text{CCl}_4$ , m. 80°,  $b_{16}$  76–7°, sol. in  $\text{H}_2\text{O}$ ,  $\text{Me}_2\text{CO}$ , EtOH and  $\text{CHCl}_3$ , somewhat sol. in  $\text{C}_6\text{H}_6$  and xylene, difficultly sol. in  $\text{CCl}_4$ , benzene, and  $\text{Et}_2\text{O}$ , stable with long boiling in  $\text{H}_2\text{O}$  or  $\text{K}_2\text{CO}_3$ , decompd. by dil. acids, gives a pale brown-red color in aq.  $\text{FeCl}_3$  and an evanescent bluish green color with Cl in  $\text{CCl}_4$ . *H* was also prepd. by shaking  $\text{ClCH}(\text{NH}_2)(\text{OEt})$  (*I*) in abs.  $\text{Et}_2\text{O}$  with  $\text{NH}_2\text{OH}$ , and the  $\text{Et}_2\text{O}$  layer evapd. *in vacuo*, and by shaking *I* in cold aq. NaOH, adding  $\text{Et}_2\text{O}$  and  $\text{ClH}_2\text{NOH}$  and proceeding as before. *H* treated with  $\text{Ac}_2\text{O}$ , extd. with  $\text{Et}_2\text{O}$ , the ext. shaken with  $\text{CaCO}_3$  and  $\text{H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4$  added, the  $\text{Et}_2\text{O}$  layer evapd., and fractionated *in vacuo*, gave the compound  $\text{MeOCON}:\text{CHOEt}$ ,  $b_{17}$  82°.  $\text{ClCH}(\text{NH}_2)\text{OMe}$  shaken in  $\text{Et}_2\text{O}$  with  $\text{NH}_2\text{OH}$  and evapd. gave the compound  $\text{HON}:\text{CHOMe}$ , needles from abs. EtOH, m. 99–100°, sol. in  $\text{H}_2\text{O}$ , somewhat sol. in cold EtOH,  $\text{Et}_2\text{O}$  and  $\text{C}_6\text{H}_6$ , difficultly sol. in  $\text{CCl}_4$  and petr. ether, gives a pale brown-red color in aq.  $\text{FeCl}_3$ , a bluish green color with Cl and decompd. by dil.  $\text{H}_2\text{SO}_4$ .  $\text{ClCH}(\text{NH}_2)\text{OC}_2\text{H}_5$  shaken in abs.  $\text{Et}_2\text{O}$  with  $\text{NH}_2\text{OH}$  gave the compound  $\text{HON}:\text{CHOC}_2\text{H}_5$ , long needles from petr. ether, m. 61–2°, sol. in  $\text{H}_2\text{O}$ , EtOH,  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$ , somewhat sol. in  $\text{C}_6\text{H}_6$ , difficultly sol. in cold petr. ether and ligroin, gives a very pale reddish yellow with  $\text{FeCl}_3$ , and a blue-green with Cl.  $\text{ClH}_2\text{NOH}$  added to a cold emulsion of aq. KOH and  $\text{Et}_2\text{O}$ , 2  $\text{HNC}:\text{HCl}$  (cf. Ber. 16, 311(1883); 31, 3852(1898)) added, salted out with  $\text{Na}_2\text{SO}_4$ , the  $\text{Et}_2\text{O}$  layer dried with  $\text{Na}_2\text{SO}_4$  and evapd. *in vacuo*, gave *formylformamidoxime*,  $\text{HON}:\text{CHNHCHO}$ , white crystals from  $\text{H}_2\text{O}$  or EtOH, m. 140° (decompn.), sol. in  $\text{Me}_2\text{CO}$ , hot  $\text{H}_2\text{O}$ , hot EtOH and NaOH (yellow color), somewhat sol. in  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$  and  $\text{CHCl}_3$ , difficultly sol. in xylene, ligroin and petr. ether, gives a brown-red  $\text{FeCl}_3$  reaction. The hydrochlorides of the formimido esters were prepd. from dry HCN, HCl and the appropriate abs. alc. in the presence of abs.  $\text{Et}_2\text{O}$ . In the method of Ziegler (cf. C. A. 15, 3256) for prepg. HCN,  $\text{K}_4\text{Fe}(\text{CN})_6$  was changed to KCN with increased yield. The free formimido esters could not be obtained from aq. HCN, the corresponding alc. and KCN.

C. C. DAVIS

**Synthesis of fats (glycerides).** C. AMBERGER AND K. BROMIG. *Biochem. Z.* 130, 252–66(1922).—The use of a high temp. is inadmissible for the prepn. of mixed glycerides of known constitution. Fischer and Pfahler's process (C. A. 15, 686) has therefore been employed.  $\alpha$ -Stearo- $\beta$ , $\gamma$ -dipalmitin, m. 63.5°, occurs in goose fat, and was prepd. from  $\alpha$ -monostearin and palmityl chloride.  $\beta$ -Stearo- $\alpha$ , $\gamma$ -dipalmitin, m. 59.1°, was prepd. from  $\alpha$ , $\gamma$ -dipalmitin, m. 69.5°. The latter is prepd. from  $\beta$ , $\gamma$ -dipalmitin- $\alpha$ -iodohydrin, m. 46.2°, by the action of  $\text{AgNO}_3$ .  $\alpha$ -Palmito- $\beta$ , $\gamma$ -distearin, m. 63.2°, was prepd. from  $\alpha$ -monopalmitin and stearyl chloride. The isomeric  $\beta$ -palmito- $\alpha$ , $\gamma$ -distearin, m. 67.9°, was prepd. from  $\alpha$ , $\gamma$ -distearin.  $\alpha$ -Palmito- $\beta$ , $\gamma$ -diolein, prepd. from  $\alpha$ -palmitin, is an oil.  $\alpha$ -Olein, a pale yellow oil, yields  $\alpha$ -oleo- $\beta$ , $\gamma$ -distearin, m. 42°.

J. C. S.

**Syntheses by means of sodamide.** A. HALLER. *Bull. soc. chim.* 31, 1073–1144

(1922).—A detailed review of various syntheses, comprizing those in which  $\text{NaNH}_2$  acts as (1) a substituent like Na with elimination of  $\text{NH}_3$ ; (2) a condensation or ring-forming agent like Na or  $\text{EtONa}$  with elimination of  $\text{NH}_3$ ; (3) a degradation agent with fixation of  $\text{NH}_3$  and (4) a ring-forming agent with fixation of N. C. C. DAVIS

A polymer of hydrogen cyanide. CH. BEDEL. *Compt. rend.* 176, 168–71 (1923).—The HCN polymer obtained by ether extr. of the crude polymerization material, repeatedly crystd. from  $\text{H}_2\text{O}$ , analyzed 44.48, 4.46, 51.97 for C, H and N, resp., whereas theory demands 44.44, 3.70 and 51.85. Mol.-wt. detns. by the b.-p. method (101.4, 118.4 and 101.4) showed the polymer to be a tetramer. It is cryst., unaffected by light when dry, m.  $179^\circ$  (decompn.). Soly. in parts per 100 by wt. at  $15^\circ$ : MeCN, 8.25; MeOH, 6.1; EtOH, 0.9;  $\text{H}_2\text{O}$ , 0.3;  $\text{H}_2\text{O}$  at  $100^\circ$  15.9. The polymer, unstable in  $\text{H}_2\text{O}$  soln., optically inactive in EtOH, yields HCN in dil. HCl and  $\text{H}_2\text{SO}_4$ ,  $\text{NH}_3$  in bases. With  $\text{Ba}(\text{OH})_2$  it yields glycocoll,  $\text{NH}_3$ ,  $\text{BaCO}_3$ ,  $\text{BaC}_2\text{O}_4$ . With alc. KOH and  $\text{CHCl}_3$  it yields carbylamine. The tetramer is therefore the hydrocyanide of aminopropanedinitrile. R. L. BROWN

Derivatives of semioxamizide. I. Ketonic semioxamazones. F. J. WILSON AND E. C. PICKERING. *J. Chem. Soc.* 123, 394–7 (1923).—Ketone derivs. of  $\text{H}_2\text{NNH-COCONH}_2$  are readily prepd. by heating the constituents in abs. EtOH on the  $\text{H}_2\text{O}$ -bath, a small amt. of I being added to accelerate the reaction in the case of the satd. ketones. These derivs. give *mono-Na* and *-K derivs.* which are very readily decompd. by  $\text{H}_2\text{O}$ . The following semioxamazones were prepd.: *acetone*, m.  $147^\circ$ ; *methyl ethyl ketone*, m.  $127^\circ$ ; *methyl isopropyl ketone*, m.  $143^\circ$ ; *methyl isobutyl ketone*, m.  $133^\circ$ ; *mesityl oxide*, m.  $163\text{--}4^\circ$ ; *benzylacetone*, m.  $125^\circ$ ; *phenyl p-tolyl ketone*, m.  $197^\circ$ . Me styryl ketone deriv. (C. A. 13, 1459) m.  $220\text{--}1^\circ$ , not  $211\text{--}2^\circ$ . C. J. WEST

Preparation and properties of triiodopyruvic acid. M. GARINO AND E. ZUNINI. *Gazz. chim. ital.* 52, II, 220–5 (1922).—Mono- and diiodopyruvic acid were required in order to complete the series of trihalogenpyruvines. Attempts to obtain these derivs. gave only triiodopyruvic acid whose prepn. is here described in detail. The introduction of I in org. compds. differs sharply from that of Cl and Br owing to the weak affinities of I for C and H. In the case of  $\text{AcCO}_2\text{H}$ , owing to the effects of CO and  $\text{CO}_2\text{H}$ , most of these processes for introducing I are useless. In attempts to iodate  $\text{AcCO}_2\text{H}$  with I in MeOH the I failed to react. Attempts to iodate with  $\text{S}_2\text{I}_2$  in the presence of  $\text{HNO}_3$  failed because the  $\text{H}_2\text{SO}_4$  formed thus:  $4\text{HNO}_3 + \text{S}_2\text{I}_2 \rightarrow 2\text{H}_2\text{SO}_4 + \text{I}_2 + 4\text{NO}$ , oxidized the  $\text{AcCO}_2\text{H}$ , giving  $\text{AcOH} + \text{HCO}_2\text{H}$ . 5 g.  $\text{AcCO}_2\text{H} + 5$  g.  $\text{H}_2\text{O} + 2$  cc. 10%  $\text{HIO}_3$  were treated with HI gas to prevent decompn. due to diln. when aq. solns. of HI were used. I presently ceased to be absorbed and  $\text{CHI}_3$  was slowly pptd. The filtrate gave  $\text{H}_2\text{C}_2\text{O}_4$ . The product decompn. thus:  $\text{Cl}_3\text{COCO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{CHI}_3 + \text{H}_2\text{C}_2\text{O}_4$ . By stopping the HI when the amt. necessary to form  $\text{CHI}_3\text{COCO}_2\text{H}$  had been added and evapg. at  $30\text{--}40^\circ$  yellowish crystals of *triiodopyruvic acid* (A) m.  $97^\circ$  (decompn.), sepd. A keeps pretty well in aq.  $\text{HIO}_3$  soln. but decompn. rapidly in light in the absence of  $\text{HIO}_3$ . For other details see the original. E. J. WITZEMANN

Trihalogenated pyruvines. M. GARINO. *Gazz. chim. ital.* 52, II, 207–20 (1922).—Fischer (*Ann.* 239, 189 (1887)) obtained tribromopyruvinate,  $\text{CBr}_3\text{COCOCONHCONH}_2$  (A) from dibromopyruvate,  $\text{CBr}_2\text{C}(\text{CO}_2\text{NH}_2)\text{CO}_2\text{NH}_2$ , by the action of  $\text{Br-H}_2\text{O}$  or

$\text{HNO}_3$ . A decompn. easily, giving  $\text{CHBr}_3$  and  $\text{NH}_4$  oxalurate when treated with dil.  $\text{NH}_4\text{OH}$ . G. was interested in prep. derivs. similar to A contg. Cl, Br and I in various combinations and proportions.  $\text{AcCO}_2\text{H}$  was converted into  $\text{CHCl}_2\text{COCO}_2\text{H}$  (B) or  $\text{CHBr}_2\text{COCO}_2\text{H}$  (C), which by treatment with  $\text{CO}(\text{NH}_2)_2 + \text{H}_2\text{SO}_4$  gave the pyruvureide. The latter was converted into the corresponding halogen pyruvinate. A 50%  $\text{H}_2\text{O}$  soln. of  $\text{AcCO}_2\text{H}$  treated with  $\text{Br}_2$  readily gave C. Anhyd.  $\text{AcCO}_2\text{H}$  was treated with  $\text{SO}_2\text{Cl}_2$  and gave  $\text{CH}_2\text{ClCOCO}_2\text{H}$  and B. 10 g.  $\text{AcCO}_2\text{H}$  were dropped slowly into

30 g.  $\text{SO}_2\text{Cl}_2$ .  $\text{SO}_2$  and  $\text{HCl}$  were evolved. The mixt. was finally warmed to  $50^\circ$  for 15 mins. On cooling *B* sepd. as a nearly white mass, m.  $57^\circ$ . At higher temps. the results were not so good. 50 g.  $\text{CO}(\text{NH}_2)_2$  + 50 g. *C* with 300 g. concd.  $\text{H}_2\text{SO}_4$  on the  $\text{H}_2\text{O}$  bath gave an 85% yield (cf. Fischer *l. c.*) of the dibromopyruvate (*D*). 20 g. *B* + 20 g.  $\text{CO}(\text{NH}_2)_2$  + 120 g. concd.  $\text{H}_2\text{SO}_4$  were heated 3 hrs. on the boiling  $\text{H}_2\text{O}$  bath. After cooling, the mixt. was poured slowly into 400 cc.  $\text{H}_2\text{O}$  by which a 90% yield of dichloropyruvate (*E*) was obtained as a powder that sublimes unchanged at  $170^\circ$  and m.  $286^\circ$ . 10 g. powdered *E* were suspended in 500 cc. boiling  $\text{H}_2\text{O}$  and treated with  $\text{Cl}$  until nearly all *E* was dissolved. On evap. the filtrate  $1/3$  a 90% yield of trichloropyruvate (*F*) was obtained in plates, m.  $242^\circ$  (decompn.). Cold dil. alkalis do not act on *F* but at  $35\text{--}40^\circ$   $\text{CHCl}_3$  is evolved. 10 g. *E* heated with 200 cc. satd. aq.  $\text{Br}_2$  gave dichlorobromopyruvate, scales, m.  $236^\circ$  (decompn.). The  $\text{Br}$  and  $\text{Cl}$  were detd. by the indirect method. 10 g. *D* in 500 cc.  $\text{H}_2\text{O}$  treated with  $\text{Cl}$  gave chlorodibromopyruvate, laminas, m.  $238^\circ$  (decompn.). 10 g. *E* in 200 cc. of 2%  $\text{HIO}_3$  were heated with 6 g. *I* in 50 cc.  $\text{CCl}_4$  6–8 hrs. under a condenser. After sepg. the  $\text{CCl}_4$  and evap. dichloriodopyruvate (*G*) seps. as yellow crystals that give violet vapors at  $150^\circ$  and m.  $230^\circ$  (decompn.). Dibromiodopyruvate was obtained like *G* from *C* as crystals that turn yellow in light, evolve *I* at  $105^\circ$  and m.  $197^\circ$  (decompn.). Compds. with more than 1 atom of *I* could not be obtained because of their instability. The trihalogenated pyruvates are all insol. in  $\text{C}_6\text{H}_6$ , in petr. ether and in  $\text{CCl}_4$ , but are sol. in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$  and  $\text{Et}_2\text{O}$ . Substitution of  $\text{Cl}$  with  $\text{Br}$  decreases their soly. and their stability in dil. alkalis. The halides  $\text{CHX}_3$  were formed by the reaction of  $\text{CX}_2\text{COCONHCONH}_2$  with dil. alkali. The pharmacological results are described elsewhere (*Arch. intern. pharmacodynamie* 26, 153(1922); *Giorn. accad. med. Torino* IV<sup>2</sup>, 19(1913)). E. J. W.

**Preparation of chlorobromiodopyruvate.** M. GARINO AND I. MUZIO. *Gazz. chim. ital.* 52, II, 226–32(1922).—The purpose of this work was to obtain chlorobromiodopyruvate (*A*), to complete the prepn. of the pyruvates obtainable and to obtain an asymm. *C* atom with 3 different halogen atoms on it. The 2 isomers have not yet been sepd. 45 g.  $\text{AcCO}_2\text{H}$  was treated drop by drop with 65 g.  $\text{SO}_2\text{Cl}_2$  in an app. adapted to prevent admission of moisture and to permit the exit of  $\text{SO}_2$  and  $\text{HCl}$ . After 48 hrs. the temp. was raised to  $35\text{--}40^\circ$  to eliminate traces of  $\text{SO}_2\text{Cl}_2$ . On cooling monochloropyruvic acid (*B*) sepd. in good yield. *B* gives anhydrous crystals that m.  $45^\circ$  and take up  $\text{H}_2\text{O}$  avidly, and rhombohedrons with 1  $\text{H}_2\text{O}$  that m.  $55^\circ$ . 10 g. *B* in 10 cc.  $\text{H}_2\text{O}$  was treated with 13.04 g.  $\text{Br}_2$  drop by drop as fast as the  $\text{Br}$  disappeared. On evap. the soln. *in vacuo*, chlorobromopyruvic acid (*C*) sepd. as deliquescent tablets, m.  $105^\circ$ . *C* +  $\text{CO}(\text{NH}_2)_2$  in equal amts. in the presence of 5 parts concd.  $\text{H}_2\text{SO}_4$  on the  $\text{H}_2\text{O}$  bath 3 hrs. gave a 90% yield of chlorobromopyruvate (*D*), m.  $120^\circ$ , when poured into 20 parts of  $\text{H}_2\text{O}$ . To 25 g. powdered *D* suspended in 750 cc. boiling  $\text{H}_2\text{O}$  13.5 g.  $\text{I}_2$  + 150 cc.  $\text{CCl}_4$  were added and then 10 g.  $\text{HIO}_3$  to keep the medium acid and to destroy the  $\text{HI}$  formed. After 12–14 hrs. the then lipid soln. was filtered, the  $\text{CCl}_4$  sepd. and the aq. soln. concd. *in vacuo* at  $40^\circ$  to remove excess *I*. On standing *A* sepd. as white crystals that evolve *I* at  $160^\circ$  and m.  $233^\circ$  (decompn.). *A* forms 20% solns. in  $\text{H}_2\text{O}$  at  $50^\circ$  and 70% solns. at  $100^\circ$  having the odor of  $\text{CHBrCl}$ . With dil. alkalis *A* gives  $\text{CHClBrI}$  which may be extd. with petr. ether. *A* is quite stable in the dry state but in soln. it loses *I* easily, especially in the light. Details concerning the detn. of the halogens are given.

E. J. WITZEMANN

**Preparation and applications of organic dithio acids.** G. BRUNT. *Giorn. chim. ind. applicata* 4, 533–4(1922).—A more convenient and economical method than those hitherto used for the prepn. of org. dithio acids is based upon a new general reaction of aldehydes, *viz.*: treatment of aldehydes with  $\text{NH}_4$  polysulfide. The latter should approx. the compn.  $(\text{NH}_4)_2\text{S}_x$  to avoid heavy deposition of free  $\text{S}$ :  $\text{RCHO} + (\text{NH}_4)_2\text{S}_x = \text{RCSS-}$

$\text{NH}_4 + \text{NH}_4\text{OH}$ . The  $\text{NH}_4$  salt is treated with an acid, e. g.,  $\text{HCl}$ , sepg. the dithio acid as a yellow, red or violet oil, and in some cases in cryst. form. The salts and the esters may be formed in the usual manner. Disulfides,  $(\text{RCSS—})_2$ , of the dithio acids are easily prepd. by oxidizing solns. of their alkali salts with solns. of  $\text{KI}$  or more economically  $\text{K}_2\text{Fe}(\text{CN})_6$ , or even oxidizing the acid by the  $\text{O}$  of the air. They are all cryst. substances. *Dithiopyromelic acid*,  $\text{O}:\text{CH}:\text{CH}:\text{CH}:\text{CCS}:\text{H}$ . Heat 10 g. furfural with

20 g. ordinary soln. of  $\text{NH}_4$  polysulfide, decant the liquid from the liberated S and acidify the filtrate with cold dil. HCl. Ext. with  $\text{Et}_2\text{O}$ . On evap. off the solvent, the acid is obtained as a violet-red oil. *Zn pyromucate*.—Dissolve the acid in NaOH, treat with  $(\text{AcO})_2\text{Zn}$ , yellow-red cryst. Use  $(\text{AcO})_2\text{Pb}$  similarly for prepn. of the purple-red needles of *Pb dithiopyromucate*. These salts are sol. in  $\text{C}_6\text{H}_6$  and PhMe, from which they can be crystall. *Disulfide of pyromucic acid*, from a soln. of the Na salt and dil.  $\text{K}_2\text{Fe}(\text{CN})_6$ , dark purple-red crystals, from  $\text{Me}_2\text{O}$ , m. 93°. The alkali polysulfides may be employed like the  $\text{NH}_4$  polysulfide, but do not give as good results. The salts and disulfides of the dithio acids may be used as powerful *vulcanization accelerators* without addn. of free S.

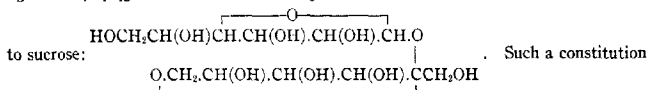
ROBERT S. POSMONTIER

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**Epiglucoamine.** P. A. LEVENE AND G. M. MEYER. *J. Biol. Chem.* **55**, 221-7 (1923).—*Monomethylepiglucoamine (A) acetate*, from triacetyl-methylglucoside 2-chlorohydrin and  $\text{NH}_4\text{OH}$ , turned brown 210°, m. 214° (cor.),  $[\alpha]_D^{20} = -130^\circ$  in 1% soln. in 2.5% HCl. *A hydrochloride*,  $[\alpha]_D^{20} = -138^\circ$  in 1% soln. in 2.5% HCl. On hydrolysis of *A* with dil. (0.25%) HCl, there was no change in  $[\alpha]$ , although the soln. now reduced Fehling soln. With stronger acid (0.5-2%),  $[\alpha]$  was decreased. With concd. HCl at room temp.,  $[\alpha]$  at first decreased, then increased beyond the original. When the products of hydrolysis with HCl of whatever concn. were evapd. *in vacuo*, crystals of a substance, decomp. 216° (cor.), believed to be *anhydroglucoamine*, were obtained. This did not reduce Fehling soln. until after hydrolysis. The reaction is indicated as 1-methylepiglucoamine  $\rightarrow$  epiglucoamine  $\rightleftharpoons$  anhydroglucoamine. *Epiglucoamine phenylosasone*,  $\text{C}_{15}\text{H}_{22}\text{N}_2\text{O}_5$ , m. 207° (cor.), sol. in warm HOAc,  $[\alpha]_D^{20} = -41^\circ$  in 1% soln. in a mixt. of 4 parts  $\text{C}_2\text{H}_5\text{N}$  and 8 parts 50% MeOH. I. GREENWALD

I. GREENWALD

**Constitution of the disaccharides. VII. Sucrose.** W. N. HAWORTH AND W. H. LINNELL. *J. Chem. Soc.* 123, 294-301(1923); cf. *C. A.* 16, 4191.—Extension of the earlier work on the constitution of sucrose (*C. A.* 14, 1821) has led to the view that the  $\gamma$ -fructose residue contains not an ethylene-oxidic but an amylene-oxidic structure. This conclusion has been reached by again submitting tetramethyl- $\gamma$ -fructose to oxidation with dil.  $\text{HNO}_3$ , the chief modification of the earlier expt. being a more prolonged digestion with this reagent. The chief product was a *trimethoxyglutarolactone*,  $b_D^{20}$  129°,  $n_D$  1.4565,  $[\alpha]_D^{20}$  18.5°, changing in 16 hrs. to 36°. After exposure to moist air, a part was transformed into a cryst. substance,  $m$  83°, which may be a polymer of the lactone or the free HO-acid. The main product of the oxidation of this lactone with alk.  $\text{KMnO}_4$  was *trimethoxyglutaric anhydride*,  $b_{D,25}$  100°, and yielding *dimethyl trimethoxyglutarate* upon treatment with  $\text{MeOH}-\text{HCl}$ ,  $b_{D,67}$  89-92°,  $n_D$  1.4419,  $[\alpha]_D^{20}$  48.7°. The following constitution is therefore to be ascribed



serves to clarify many of the existing anomalies in the literature of  $\gamma$ -sugars. **VIII. Sucrose.** W. N. HAWORTH AND J. G. MITCHELL. *Ibid* 301-10.—Continuing the above work, tetramethyl- $\gamma$ -fructose (*A*) has been oxidized with  $\text{KMnO}_4$ , containing a small amt. of  $\text{NaOH}$ , the main product being dimethoxybutyrolactone,  $b_{D-14}$  130-5°,  $n_D$  1.4419; the ox-

dation product was also isolated as the K salt.  $\text{Br-H}_2\text{O}$  did not oxidize *A*. When *A* is dissolved in MeOH contg. 0.25% HCl (concn. of *A*, 2.4%) there is a const. increase of  $[\alpha]_D^{15}$  from 19.9° to 57.7° during 7200 min. After 1700 min. ( $[\alpha]$  49.8°) the soln. was not reactive towards Fehling soln. Heated to 35°, a temporary fall in rotation was observed, but the higher value was restored upon cooling to room temp. The product  $b_{13}$  137-9°,  $n_D$  1.4461, and showed  $[\alpha]_D^{18}$  48.8° ( $\text{H}_2\text{O}$ , *c* 2.42); 38.7° (EtOH, *c* 2.95); 40.0° (MeOH, *c* 2.32). It has been found that by conducting the 2nd and 3rd methylations of sucrose in much more dil. solns. and using a larger excess of  $\text{Me}_2\text{SO}_4$  and NaOH, the octa-Me deriv. can be obtained without the use of MeI. The 2 products of hydrolysis can be readily sepd. by taking advantage of the fact that *A* readily condenses with MeOH at room temp. while the glucose residue requires prolonged digestion at a higher temp. to effect this condensation. Reduction of *A* by Na-Hg in moist EtO gave a product,  $\text{C}_{10}\text{H}_{20}\text{O}_6$  (mixt. of tetramethylmannitol and sorbitol),  $b_D$  171°,  $n_D$  1.4572,  $[\alpha]_D^{15}$  10.8°. In the hydrolysis of heptamethylsucrose there was isolated a cryst. trimethylglucose, m. 124°,  $[\alpha]$  changing from 118.4° to 69.3° in 24 hrs.; this is identical with the product obtained by Haworth and Leitch. The bearing of these facts upon the new formula for sucrose is discussed.

C. J. WASS

**A magnesyl derivative of cellulose.** D. COSTA. *Gazz. chim. ital.* 52, II, 362-5 (1922).—Oddo (*C. A.* 14, 1529) in discussing the constitution of cellulose pointed out that its behavior with bland reagents should be studied. In this paper its behavior with  $\text{MgBrEt}$ , which is a valuable reagent for active H (cf. *C. A.* 5, 2639), is described. The cellulose used was especially prepd. from ashless filters.  $\text{MgBrEt}$  (from 2.4 g. Mg + 10.8 g. EtBr) in EtO was heated on the  $\text{H}_2\text{O}$  bath with 1.6 g. cellulose for 24 hrs.  $\text{C}_2\text{H}_4$  was evolved. For analysis the excess  $\text{MgBrEt}$  soln. was drained off and the gray-green solid portion rapidly transferred to a Soxhlet extractor and extd. with EtO 1 hr. The Mg and Br contents of the product corresponded to  $\text{C}_6\text{H}_8\text{O}_5\text{MgBr}(\text{EtO})$ , i. e., a monobromomagnesium derivative of cellulose (*A*) with 1 mol. of EtO of constitution. *A* has a very great avidity for  $\text{H}_2\text{O}$ , in which it undergoes decompn., giving unchanged cellulose and  $\text{MgBrOH}$ . On the basis of the  $\text{C}_2\text{H}_4$  evolved and the compn. of *A* there are not 3 OH groups in cellulose as required by Green's formula but only 1 OH group. This suggests that 2 of the O atoms up till now considered as belonging to OH groups do not function in this way.

E. J. WITZEMANN

**Oxidation of amyloextrin.** WIKTOR SYNIEWSKI. *Roczniki Chem.* 2, 83-94 (1922).—When amyloextrin (sol. starch) is oxidized by means of Br in the presence of  $\text{BaCO}_3$  (to prevent the hydrolysis of the mol.), amyloextrinic acid,  $\text{C}_{212}\text{H}_{340}\text{O}_{198}$ , is obtained as a white, non-cryst. substance. It has an acid reaction,  $[\alpha]_D^{20}$  191.09°, and its reducing power is 23.24% of that of maltose. In soln., it reduces alk. Ag soln. and gives the "Molisch" reaction with  $\alpha$ -naphthol, but the color is not violet as with starch and the sugars, but carminic-red. In concd. soln., it gives a red color on warming with  $\text{NH}_4\text{OH}$ , HCl and KOH. S. assumes that amyloextrin has the formula  $\text{C}_{204}\text{H}_{328}\text{O}_{186}$  and contains 12 maltose residues connected together by the CO groups, and that the  $\text{CH}_2\text{OH}$  groups alone undergo oxidation to  $\text{CO}_2\text{H}$  groups.

J. C. S.

**Chemistry of the glutamic acids. XIV. Three-carbon tautomerism in the cyclopropane series.** F. R. GOSS, C. K. INGOLD AND J. F. THORPE. *J. Chem. Soc.* 123, 327-61 (1923); cf. *C. A.* 15, 2070.—Because of certain abnormal reactions, it seemed desirable to investigate the behavior of certain cyclic substances possessing a structure similar to that of glutamic acid, in order to ascertain whether the phenomena associated with this particular group are of widespread occurrence. 3-Methyl- $\Delta^2$ -cyclopropene-1,2-dicarboxylic acid (*A*) was selected. Its prepn. is reported in detail by steps. Although only 1 acid is isolable, evidence of a "labile phase" is seen in the formation of a *hydroxy anhydride*,  $b_D$  185-90°, by the action of  $\text{Ac}_2\text{O}$ . Three types of esters re-



subt: normal, labile and enol. The *normal ester* was obtained by direct esterification of the acid with EtOH, by digesting the Ag salt with EtI, by heating either the labile or enol ester in EtOH contg.  $\text{H}_2\text{SO}_4$ , by keeping the 2 esters at the ordinary temp. for 1-2 yrs., or by treating these esters with EtONa for 2 days at  $60^\circ$ . The *normal ester* may be sepd. from the mixt. with the labile isomer by freezing out at  $-40^\circ$ , by fractional distn. under 20 mm. (the labile ester b.  $20^\circ$  higher), or by means of dil. EtONa, which at once reacts with the labile ester. The *normal ester* is sepd. quant. from the enol ester by shaking with 10% aq. KOH. Distn. under atm. pressure converts the *normal ester* into the labile ester. The *labile ester* results in 5% yield in the esterification of the acid, also from the *normal ester* by heating with EtOH and  $\text{H}_2\text{SO}_4$  or by distn. under atm. pressure and from the enol ester by standing, by acid catalysis at ordinary temp. or by heating. The *labile ester* is sepd. from the enol ester by extg. the latter with dil. alkali. The *enolic ester* is formed in small amts. in the direct esterification of the acid, by heating either of the other esters with EtOH and  $\text{H}_2\text{SO}_4$  or by distn. of the *normal ester* under atm. pressure or the *labile ester in vacuo*, in 60% yield by the action of hot concd. EtONa upon the *normal ester* and quant. by the action of cold dil. EtONa upon the *labile ester*. Each of the 3 esters, heated in EtOH contg.  $\text{H}_2\text{SO}_4$ , gave a mixt. of the 3 esters in the same proportion as obtained upon esterification of the acid. The ratio of *normal* and *enol* esters and of ethoxy acid obtained upon treatment of each ester with EtONa is also reported. The *normal methyl ester*, m.  $33-4^\circ$ ,  $b_{30}$   $122^\circ$ , is transformed under 782 mm. into the *labile ester*,  $b_{30}$   $135^\circ$ . The products of the action of  $\text{O}_3$  upon the *normal* and *labile ester* were the same,  $\text{AcCH}(\text{COCO}_2\text{Et})\text{CO}_2\text{Et}$  being isolated from the decompd. ozonide. Na-Hg did not reduce the free acid; heated under a reflux with HI, *labile*  $\beta$ -methylglutaconic acid was obtained, while in a sealed tube at  $180^\circ$  the *normal acid* (B) was also found. The action of Br and HOBr is reported, the products being the same as those prepd. by Feist (C. A. 16, 2307). *Methyl 3-methoxy-3-methylcyclopropane-1,2-dicarboxylate*, m.  $98^\circ$ . The *methyl hydrogen ester*, m.  $136^\circ$ , is obtained if the reaction product is boiled for 2 hrs. *3-Ethoxy-3-methylcyclopropane-1,2-dicarboxylic acid*, m.  $156^\circ$ , is reduced to B by HI. Oxidation of A by alk.  $\text{KMnO}_4$  gave  $(\text{CO}_2\text{H})_2$ . A lengthy theoretical discussion is given. C. J. WEST

An optical study of mixed crystals of ammonium and potassium Seignette salts. L. BACUVIER. *Bull. soc. franç. mineral.* 45, 73-85 (1922).—The values  $\alpha$ ,  $\beta$ , and  $\gamma$  for mixed crystals of  $\text{NH}_4\text{NaC}_4\text{H}_4\text{O}_6$  and  $\text{KNaC}_4\text{H}_4\text{O}_6$  are tabulated for 6 wave lengths of light and several compns. Measurements and curves are presented showing the variation of  $2V$  with compn. The K salt has (010) as the optic axial plane and is +; the  $\text{NH}_4$  salt, (100) and —. The dispersion is so strong that the compn. for the uniaxial pt. varies greatly with the light used; for  $625 \mu\mu$  it is at 34%  $\text{NH}_4$  salt; for  $436 \mu\mu$ , at 60%. E. F. H.

Configuration of the doubly linked tervalent nitrogen atom. The resolution of the pyridylhydrazone of cyclohexylene dithiocarbonate. W. H. MILLS AND HANS SCHINDLER. *J. Chem. Soc.* 123, 312-23 (1923); cf. C. A. 4, 1156; 5, 479.—In continuing the earlier work it seemed desirable to investigate some other compd. of as different a chem. type as possible from 4-hydroximinocyclohexanecarboxylic acid but possessing the same stereochem. characteristics that its mol. is asym. or not according as the 3 valences of the doubly linked N atom have a trihedral or a planar distribution. *Cyclohexylene trithiocarbonate*, from 2-iodocyclohexanol and  $\text{K}_2\text{CS}_3$ , m.  $165-6^\circ$  (11% yield). *Phenylhydrazone*, m.  $181.5-2^\circ$ . *2-Pyridylhydrazone* (A), yellow, m.  $187-8.5^\circ$ . The alc. mother liquors contain *benzoisotriazolyl mercaptan*, m.  $205-6^\circ$ , also obtained by the action of  $\text{H}_2\text{CS}_3$  on  $\text{C}_6\text{H}_5\text{N}(\text{C}_6\text{H}_5)_2$ . Oxidation yields benzoisotriazole. Resolution of A with *d*-bromocamphorsulfonic acid showed that while the resolution was effected, no regularity could be secured in fractionation. This was finally carried out by pptn.

from EtOH by Et<sub>2</sub>O, the fractions with  $[\alpha]_D$  higher than 67° or lower than 36° being combined. In this way fractions with  $[\alpha]$  of 82° and of 8.6° were finally secured. Upon decompn. the higher fraction gave an optically active *A*, m. 168–9°,  $[\alpha]_D^{25}$  46.3°; the 2nd fraction likewise m. 168–9° and showed  $[\alpha]_D^{18}$  –83°. The optically pure enantiomerides probably possess considerably larger sp. rotations. Values of 131° and –100° are recorded but these products were not analyzed. These observations show that in several different types of compds. the valencies of a doubly linked N atom have a trihedral disposition.

C. J. WEST

*m*-tert-Amyltoluene (3-tert-amyl-1-methylbenzene). G. CHARRIER, M. GALLOTTI AND E. ZAPPELLI. *Gazz. chim. ital.* 52, II, 317–23 (1922).—*iso*-AmCl acting on PhMe in the presence of Zn dust gave amyltoluene (Pabst, *Bull. soc. chim.* [2] 25, 337 (1876)), b. 203–5°, not identical with the product, b. 203°, obtained from AmBr + *p*-BrC<sub>6</sub>H<sub>4</sub>Me + Na (Fittig, Bigot, *Bull. soc. chim.* [2] 8, 346 (1867)). Essner and Gossin (*Bull. soc. chim.* [2] 42, 213 (1884)) obtained from PhMe + AlCl<sub>3</sub> and MeEtCHCH<sub>2</sub>Cl, Me<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>Cl or Me<sub>2</sub>C:CHMe the same amyltoluene, b. 200–5°, which they considered to be *tert*-m-amyltoluene (*A*). C. thought that the constitution of *A* could be settled by the action of AlCl<sub>3</sub> on PhMe + Me<sub>2</sub>EtCCl, which gave HCl + *A*. No isomerization occurs in such cases (Egorov, *J. Russ. Phys.-Chem. Soc.* 30, 1031–5 (1898)). Me<sub>2</sub>EtCCl, b. 86° (obtained by satg. dry Me<sub>2</sub>EtCOH with HCl gas), in excess PhMe was treated gradually with 30 g. AlCl<sub>3</sub> per g. mol. and finally warmed on the H<sub>2</sub>O bath. *A* was sep'd. by pouring the mixt. on ice and fractionating the upper layer; *A* smells like pine resin, b. 208–9°,  $d_4^{20}$  0.8930,  $d_4^{25}$  0.8673 (d. also given for 10 other temps.) *A* oxidized with KMnO<sub>4</sub> in H<sub>2</sub>O according to Ullmann (*Ber.* 36, 1797 (1903)) gave isophthalic acid (*B*); *A* + 9 O<sub>2</sub> → *B* + 6 H<sub>2</sub>O + 4 CO<sub>2</sub>. The oxidation requires several days on the H<sub>2</sub>O bath. 22 g. *A* boiled under a condenser 10 hrs. with 550 cc. dil. HNO<sub>3</sub> (1:3) gave *B* instead of the *m*-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CM<sub>2</sub>Et desired. 29 g. *A* were dropped slowly into 87 g. fuming HNO<sub>3</sub> (d. 1.52) at –10°. The product poured on ice gave an oil, which in Et<sub>2</sub>O soln. was freed from acid with dil. NaOH. The product on fractionation gave 2 isomeric *mononitro* derivs. of *A*, b<sub>75</sub> 160–1°,  $d_4^4$  1.0675, and b<sub>75</sub> 165–9°,  $d_4^4$  1.0825. Both are bright yellow liquids and could not be crystd. *A* + 5% I<sub>2</sub> was treated with the calcd. amt. of Cl<sub>2</sub> at 0°. The product was washed with H<sub>2</sub>O, neutralized with dil. NaOH, decolorized with NaOCl, dried with CaCl<sub>2</sub> and fractionated. 2 fractions were obtained: b<sub>75</sub> 242–3°,  $d_4^4$  0.9769, and b<sub>75</sub> 247–8°,  $d_4^4$  1.0111. Both are *monochloro* derivs. and by analogy with the xylene derivs. obtained by Jacobsen (*Ber.* 18, 1760 (1885)) the Cl is substituted *p*- to the Me and Am groups, resp. Br<sub>2</sub> acting on *A* in the dark without catalyzer when the product was worked up as with the Cl derivs. gave the *monobromo* derivs. of *A*, b<sub>75</sub> 262–4°, d. 1.2143, in which the Br is probably substituted *p*- to the Me or Am group.

E. J. WITZEMANN

Reactivity of doubly conjugated unsaturated ketones. IV. The effect of substitution on the reactivity of 4'-dimethylamino-2-hydroxydistyryl ketone. I. M. HELLBRON AND A. B. WHITWORTH. *J. Chem. Soc.* 123, 238–45 (1923); cf. *C. A.* 16, 90; 17, 98.—In order to test the validity of the views earlier expressed, the effect of substitution in the phenolic residue of the mol. has been studied. Neither by the introduction of basic nor of acidic groups into the mol. is the reactivity increased. The 5-MeO deriv. is practically as reactive as the unsubstituted ketone but the 3-MeO deriv. is much less reactive, while the 4-MeO deriv. is totally unreactive. This behavior is considered as a strong support of the earlier views. 5-Nitro-2-hydroxydistyryl methyl ketone, from 5-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>(OH)CHO in 2 *N* NaOH and AcMe, yellow, m. 227°; with *p*-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO this yields 5-nitro-4'-dimethylamino-2-hydroxydistyryl ketone, dark red, contg. 1 EtOH of crystn., m. 238°. 5-Bromo deriv., from the 5-Br ketone, orange, m. 194°. The additive compd. with 1 EtOH is crimson with violet luster; with 1 C<sub>6</sub>H<sub>5</sub>

red; with 1 EtOAc, orange; with 1 CHCl<sub>3</sub>, green; with 0.5 CHCl<sub>3</sub>, yellow. *3-Methoxy-2-hydroxystyryl methyl ketone*, pale yellow, m. 83°, contains 1 H<sub>2</sub>O which is not split off by boiling in C<sub>6</sub>H<sub>6</sub> with P<sub>2</sub>O<sub>5</sub> or Ac<sub>2</sub>O. With BzCl, however, is obtained a *monobenzoate*, m. 120°. *4'-Dimethylamino deriv.*, bright red, m. 151°, if crystd. from EtOH or violet, m. 165°, from C<sub>6</sub>H<sub>6</sub>; the latter probably contains C<sub>6</sub>H<sub>6</sub> of crystn. as on exposure to air it becomes crimson. Crystn. from CHCl<sub>3</sub> gives a mixt. of green and orange crystals, which rapidly lose CHCl<sub>3</sub>, forming the red product, m. 165°; this can be converted to the lower m. form by crystn. from EtOH. *4-Methoxy-2-hydroxystyryl methyl ketone*, pale yellow, m. 131°. *4'-Dimethylamino deriv.*, purple, m. 182°, results only by the use of 50% NaOH. No additive compds. were observed. *5-Methoxy-2-hydroxystyryl methyl ketone*, bright yellow, m. 122°. *4'-Dimethylamino deriv.*, obtained as the *p*-dimethylaminobenzaldehyde addition product, bright red, m. 110°; boiled with C<sub>6</sub>H<sub>6</sub>, the greenish purple benzene addition product, m. 120°, resulted; heating this gives the free ketone, dark crimson, m. 151°. *Ethyl acetate addition product*, black glistening crystals.

C. J. WEST

**Preparation of aromatic chloromethylene derivatives.** G. BLANC. *Am. Perfumery* 17, 541-2; *Perfumery Essent. Oil Record* 14, 40-2(1923).—Expts. are described showing the action of HCl on various aromatic hydrocarbons in the presence of (CH<sub>3</sub>O)<sub>2</sub> or formalin, and powdered ZnCl<sub>2</sub>. Thus, with C<sub>6</sub>H<sub>6</sub>, PhCH<sub>3</sub>Cl and *p*-C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>Cl)<sub>2</sub> were isolated, the former in about 80% of the theory. PhMe yielded mainly *p*-MeC<sub>6</sub>H<sub>4</sub>-CH<sub>2</sub>Cl, in considerably less amt. MeC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>Cl)<sub>2</sub>, probably in 2 isomeric forms (1,3,4 and 1,2,4). From *m*-xylene, chloromethylxylene (1,3,4) and dichloromethylxylene (1,3,4,6) were prepd. EtPh gave *p*-EtC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl; PrPh, *p*-PrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl; PhCl, *p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl; cymene, 1,2,4-C<sub>7</sub>H<sub>3</sub>Me(CH<sub>2</sub>Cl)Pr; and C<sub>10</sub>H<sub>8</sub>,  $\alpha$ -C<sub>10</sub>H<sub>7</sub>CH<sub>2</sub>Cl.

W. O. E.

**Catalytic reduction of nitro, azo, etc., derivatives.** ANDRÉ BROCHET. *Bull. soc. ind. Mulhouse* 88, 703-7(1923).—Sealed note No. 2197, deposited Aug. 8, 1912.—B. extends catalytic hydrogenation to compds. in soln. or in suspension in suitable solvents or media, thus applying it to compds. which could not be vaporized without decompn. The method is suitable for the hydrogenation of both the C<sub>6</sub>H<sub>5</sub> nucleus and the substituted groups (especially NO<sub>2</sub>, etc.), at any suitable temp. (generally 100-150°, but below 100° in certain cases) and pressures up to 10-15 kg. per cm.<sup>2</sup>. Direct reduction of nitro and azo compds. gives corresponding amines; but reduction in alk. soln. gives azoxy, hydrazo, etc., compds. Suitable solvents are AmOH and cyclohexanol, the latter being obtainable from PhOH by this process. Several examples are given. **Report by M. Battegay.** *Ibid* 707-8.—Brochet had already referred to the results described in note No. 2197 (*C. A.* 7, 2703; 8, 3180), but has not described the expts. in detail as he does in the note. Sealed note 2879 of Oct. 2, 1913 is a true copy of the specifications of Fr. patent 473,536 applied for Sept. 29, 1913.

A. PAPINEAU-COUTURE

**New research on the capacity of formation of phenylhydrazones.** BERNARDO ONDO AND LUIGI PIATTI. *Gazz. chim. ital.* 52, II, 333-46(1922).—The results obtained in previous work (*C. A.* 8, 667; 9, 2525) on the cryoscopic study of the reaction: dry PhNHNH<sub>2</sub> + CO deriv.  $\rightarrow$  H<sub>2</sub>O + phenylhydrazone suggested the examination of compds. with more complex mols. in this way. In the following the time required to obtain a constant f. p. is given in mins., but if in parentheses the reaction was incomplete, if it had begun. The observed mol. wt. is given first and then the calcd. mol. wt. followed by the time in mins. The compds. tested and the results obtained are summarized thus: acetone 30.86, 58.04 in 21'; diacetyl 44.56, 86.04 in 26'; acetylacetone 36.09, 100.06 in 75'; dibenzoyl 67.77, 210.08 in 200'; dipyrrolyl (169.97), 188.08 in (102'); anthraquinone—, 208.16 in —; camphor (106.08), 152.12 in (125'); bromocamphor (220.90), 231.08 in (158'); fenchone (138.48), 152.12 in (141'); carvone (142.92), 150.11

in (91'); pulegone (79.85), 152.12 in (146'); menthone (92.21), 154.14 in (272'); santonin (250.33), 246.14 in (78'); glucose 90.51, 180.09 in 75'; cuminal 81.08, 148.09 in 11'; phenylacetaldehyde 56.12, 120.06 in 36'; *o*-nitrobenzaldehyde 73.08, 151.05 in 38'; *m*-nitrobenzaldehyde 74.79, 151.05 in 48'; *p*-nitrobenzaldehyde, 81.31, 151.05 in 7'; cinnamaldehyde 60.77, 132.06 in 12'; *m*-nitrocinnamaldehyde 87.50, 177.06 in 6'; vanillin 76.48, 152.06, in 8'; *p*-dimethylaminobenzaldehyde 75.25, 149.09 in 6'; furfural 49.55, 97.03 in 32'; *o*-phthalic aldehyde 30.79, 134.04 in 43'. The proportions used were 100 mols. PhNHNH<sub>2</sub> per mol. of the CO compd. The results show that Ac<sub>2</sub> reacts at once with PhNHNH<sub>2</sub> giving the monophenylhydrazone: the osazone is formed very slowly. Anthraquinone gave soly. troubles. CH<sub>3</sub>Ac<sub>2</sub> reacts almost instantaneously with PhNHNH<sub>2</sub> and the data show a lowering corresponding to 3 cryoscopic particles (2 mols. H<sub>2</sub>O and 1 of a phenyldimethylpyrazole). The results with Bz<sub>2</sub> were similar but the reaction was considerably slower. Dipyrrolyl does not react at all with dry PhNHNH<sub>2</sub>. The terpene ketones, camphor, bromocamphor and fenchone, are all inert toward dry PhNHNH<sub>2</sub> but pulegone reacts completely at a fairly const. rate for 90' and then at a decreasing rate. Menthone reacts still more slowly but in the same way as pulegone. Carvone, which, because of its unsatd. bonds, can undergo enolization, is inactive. The remaining compds. tested were all aldehydes which reacted quickly with dry PhNHNH<sub>2</sub>. The aldehydes in general react more quickly than any ketones except the cyclohexanic ketones. The complete data are given in tables and are plotted in graphs.

E. J. WITZEMANN

**Cryoscopic investigation of the capacity of formation of Schiff bases.** BERNARDO ODDO and FRANCESCO TOGNACCHINI. *Gazz. chim. ital.* 52, II, 347-61 (1922).—Cryoscopic studies with various solvents have helped to establish the relations that exist between the solvent and the solute and have confirmed the value of the method for detg. mol. wts. An essential condition is indifference between the solvent and the dissolved substance. But f.-p. detns. also offer a method of following the progress of certain chem. reactions. O. has studied the action of PhNHNH<sub>2</sub> (*C. A.* 8, 84; 9, 2525, and preceding abstr.) on C:O derivs. in this way and detd. marked differences in the velocity of formation of the phenylhydrazones. Of the various other solvents that could be selected that react with various compds. PhNH<sub>2</sub>, which reacts to give Schiff bases with aldehydes and ketones at room temp. thus: PhCHO + PhNH<sub>2</sub> → H<sub>2</sub>O + Ph-CH:NPh, was selected for further study. The numerical data are given in tables and the results are discussed in connection with graphs in which the results are plotted. It is evident at once that PhNH<sub>2</sub> reacts much more slowly than PhNHNH<sub>2</sub> in forming the group CH:N and therefore brings out differences in behavior that the latter does not show. Thus *o*-, *m*- and *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO show decreasing velocity of reaction with PhNH<sub>2</sub> in the order given, which the reaction with PhNHNH<sub>2</sub> is too rapid to show. *p*-MeC<sub>6</sub>H<sub>4</sub>CHO reacts with PhNH<sub>2</sub> rapidly like all aromatic aldehydes, while the isomeric PhCH<sub>2</sub>CHO reacts slowly. Cinnamic aldehyde (*A*) reacts more rapidly than either of the 2 preceding compds. The *m*-NO<sub>2</sub> deriv. (*B*) of *A* reacts more slowly than *A* but the *m*-NO<sub>2</sub> deriv. (*C*) of BzCHO reacts much more slowly even than *B*. BzCHO reacts faster than *A* with PhNH<sub>2</sub>. The velocity of reaction decreases with *A*, anisaldehyde, vanillin and piperonal in the order given. The velocity of reaction of Ph<sub>2</sub>CO, Me<sub>2</sub>CO, Bz<sub>2</sub>, CH<sub>3</sub>Ac<sub>2</sub> and (CH<sub>3</sub>Ac)<sub>2</sub> (*D*) with PhNH<sub>2</sub> decreased in the order given but was in all cases very slow. The results for *D* indicate that *N*-phenyl- $\alpha,\alpha$ -dimethylpyrrole (Paal, *Ber.* 19, 551) + 2H<sub>2</sub>O, are formed. 3 terpenic ketones were studied: camphor is inactive with PhNH<sub>2</sub> and carvone and menthone react very slowly. The velocity of reaction of *o*-, *m*- and *p*-methylcyclohexanone increased in the order given while that of cyclohexanone was intermediate. Phenanthrenequinone acts distinctly but slowly with PhNH<sub>2</sub>; santonin reacts still more slowly. Phenolphthalein

reacts instantly, giving the anilide. The f. p. of  $\text{PhNH}_2$  is given variously in the literature owing to its tendency to absorb  $\text{H}_2\text{O}$  and  $\text{O}_2$ . After recrystg. twice from  $\text{Et}_2\text{O}$  and distg. under 10 mm.  $\text{PhNH}_2$  (sealed in ampules) m.  $-6.26^\circ$  to  $-6.21^\circ$  when used. The f.-p. const. used was  $K = 53.7$ . The f.-p. app. was previously described (C. A. 12, 1137). The details of the manipulations of the f.-p. detns. are described.

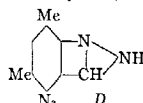
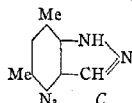
E. J. WITZEMANN

**The isonitriles. IV. Reaction with organic acids.** M. PASSERINI. *Gazz. chim. ital.* 52, II, 250-7 (1922).—P. previously described (C. A. 16, 556) the reaction between aromatic isonitriles (A) and aldehydes, ketones and org. acids giving arylamides of acylated  $\alpha$ -HO acids. In this paper P. studies the action of org. acids upon A. At ordinary temp. A gives with org. acids substituted formamidine salts,  $\text{PhN}:\text{CHNHPh}\cdot 2\text{RCO}_2\text{H}$ . The formation of arylformamidine may be considered as a first step in the hydration of isonitriles. These first products are easily obtained in working with acids whose salts with the formamidine are little sol. and are removed from further action of the acid itself by being pptd. The product with  $\text{AcOH}$ , however, is sol. and is sapond. to the formyl deriv. and amine. In the reaction between A and org. acids CO or  $\text{HCO}_2$  should be formed. P. found CO and the reaction is thus:  $2\text{PhNC} + \text{H}_2\text{O} + 2\text{RCO}_2\text{H} \longrightarrow \text{PhN}:\text{CHNHPh}\cdot 2\text{RCO}_2\text{H} + \text{CO}$ . Similarly picric acid acting on  $\text{PhNC}$  gives *diphenylformamidine picrate* (B).  $\text{PhNC}$  treated with  $\text{HCl}$  in  $\text{Et}_2\text{O}$  gave *diphenylformamidine hydrochloride* (C). The compd.  $(\text{PhN}:\text{CHCl})_2\cdot\text{HCl}$  obtained by Nef (*Ann.* 270, 303) may be an earlier stage but was not observed. 1.5 g.  $\text{PhNC} + 1.75$  g. mandelic acid in cold  $\text{Et}_2\text{O}$  yielded in 2 days 1 g. *diphenylformamidine mandelate* (D), needles, m.  $126^\circ$ . 1.5 g. D suspended in  $\text{H}_2\text{O}$  were agitated 1 hr. with excess  $\text{NH}_4\text{OH}$  and gave 0.7 g. *diphenylformamidine* (E), m.  $138-9^\circ$ . Mandelic acid was isolated as the Ag salt from the filtrate. The lactate of E,  $\text{PhN}:\text{CHNHPh}\cdot 2\text{MeCH}(\text{OH})\text{CO}_2\text{H}$  (F), obtained as with D, needles, m.  $136^\circ$ . F agitated for some time with  $\text{H}_2\text{O}$  loses  $1/2$  its acid, giving the *monolactate* of E, needles, m.  $151^\circ$ . The *salicylate*, m.  $165^\circ$ , and *benzoate*, m.  $175-6^\circ$ , of E were similarly prepd. 2 g. *p*- $\text{PhN}:\text{NC}_6\text{H}_4\text{NC}$  were dissolved in 5 g. lactic acid. After 12 hrs.  $\text{Et}_2\text{O}$  was added and 1.2 g. *4,4'*-bisazobenzeneformamidine lactate (G),  $\text{PhN}_2\text{C}_6\text{H}_4\text{N}:\text{CHNHC}_6\text{H}_4\text{N}_2\text{Ph}\cdot 2\text{MeCH}(\text{OH})\text{CO}_2\text{H}$ , were obtained as yellow scales, m.  $163^\circ$ . G agitated 15 mins. with  $\text{NH}_4\text{OH}$  gave *4,4'*-bisazobenzeneformamidine, yellow needles, m.  $196-7^\circ$ . 2 g.  $\text{PhNC}$  added to 4.5 g. picric acid in  $\text{C}_6\text{H}_6$  pptd. B,  $\text{PhN}:\text{CHNHPh}\cdot\text{C}_6\text{H}_3(\text{OH})(\text{NO}_2)_3$ , as yellow acicular crystals, m.  $187^\circ$ . 5 g.  $\text{PhNC} +$  an equal vol. of  $\text{Me}_2\text{CO}$  were treated drop by drop with a satd.  $\text{Me}_2\text{CO}$  soln. of  $\text{HCl}$  gas. Gas was evolved and C pptd. as long needles, m.  $245^\circ$ . *4,4'*-Bisazobenzeneformamidine hydrochloride was obtained as with C as a yellow compd.

E. J. WITZEMANN

**Upper limits of diazotizability in the benzene series.** Diazo derivatives of mesitylene. G. T. MORGAN AND G. R. DAVIES. *J. Chem. Soc.* 123, 228-37 (1923).—The problem was to det. whether the aromatic nucleus can carry at one time more than 2 diazonium radicals; the answer appears to be that it does not readily do so. The existence of aromatic diazonium salts is certainly connected with the unsatd. character of the aromatic nucleus, and although this unsatn. suffices to give permanence to 1 or even 2 diazonium complexes, it is apparently insufficient to confer stability on a 3rd diazonium radical. Nitromesidine yields *nitromesitylenediazonium chloride* (A), which was identified by conversion into the *chloroaurate*, greenish yellow, intumescing without m., and the *dichromate*, bright crocus-yellow, turning brown on exposure to light and exploding on gentle heating. The *azoimide* (*triazoniomesitylene*) results upon treatment of A with  $\text{NaN}_3$ ; from moist  $\text{Et}_2\text{O}$  it crystals with 1  $\text{H}_2\text{O}$ ;  $1/3$  of the N is lost with concd.  $\text{H}_2\text{SO}_4$ . *Nitromesityleneazo- $\beta$ -naphthol*, red, m.  $168^\circ$ ; it gives a purple color with concd.  $\text{H}_2\text{SO}_4$ . The *acetacetanilide deriv.*,  $\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_4$ , yellow, m.  $171^\circ$ . Attempts to

prep. triazaoaminomesitylene by the partial diazotization of diaminomesitylene (B) followed by treatment with  $\text{NaN}_3$ , always gave triazomesityleneindazole, (C or D), yellow m.  $134-7^\circ$ . In the diazotization of B, an excess  $\text{NaNO}_2$  is necessary to produce the disazo deriv. Aminomesityleneazo- $\beta$ -naphthol, crimson, m.  $173^\circ$ . Mesitylenebisdiazonium chloroaurate, light brown. The dichromate is yellow, darkens in the light and explodes on slight friction. Bistriazomesitylene, yellow oil with fruity odor, which intumesces



on heating and evolves white fumes with concd.  $\text{H}_2\text{SO}_4$ . Nitroaminomesitylenediazonium chloroaurate hydrochloride,  $\text{C}_9\text{H}_{10}\text{O}_2\text{N}_4\text{Cl}_3\text{Au}$ , brown. Nitroaminomesityleneazo- $\beta$ -naphthol, brown, m.  $208-9^\circ$ . The resorcinol deriv. is bright crimson and did not m.  $290^\circ$ . Triazonitroaminomesitylene, light yellow, m.  $83-4^\circ$ . The HCl soln. can be diazotized and yields a brown ppt. with  $\beta\text{-C}_{10}\text{H}_7\text{OH}$ . Bistriazomitroaminomesitylene, light yellow, m.  $50^\circ$ . Bistriazohydroxymesitylene,  $\text{Me}_3\text{C}_6(\text{OH})(\text{N}_3)_2$ , m.  $67^\circ$ . This gives a deep red color with  $\text{FeCl}_3$ , which is discharged by acids. Aminomesitylenebisdiazonium chloroaurate hydrochloride, light brown, explodes on gentle warming. This may be diazotized in excess HCl and yields a triazonium chloroaurate hydrochloride, which explodes on warming. Bistriazomesidine, m.  $68^\circ$ . Tristriazomesitylene,  $\text{C}_9\text{Me}_3(\text{N}_3)_3$ , m.  $50^\circ$ , was obtained by diazotization, treatment with  $\text{NaN}_3$  and repetition of the operations. C. J. W.

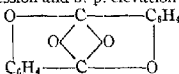
Synthetic vanillin manufacture. BURTON G. WOOD. *Chem. Met. Eng.* 28, 399 (1923).—The properties of pure vanillin are discussed. Many of the numerous patents for the synthetic manuf. are useless, and the objections to a number of them are given. Two processes are more promising than the rest. They consist in the oxidation of isoeugenol (1) by  $\text{PhNO}_2$ , and (2) by  $\text{O}_3$ , using a protecting agent for the vanillin formed. W. will discuss these methods in later articles. E. H. VOLWILER

Addition of bromine to the  $\alpha$ - and  $\beta$ -chloro- and bromocinnamic acids and their esters. J. J. SUDBOROUGH AND GWYLYM WILLIAMS. *Indian Inst. Sci.* 5, 107-18 (1923).—According to the equations 1.  $\text{PhCH:CClCO}_2\text{H} + \text{Br}_2 \rightarrow \text{PhCHBrCClBrCO}_2\text{H}$ ; 2.  $\text{PhCH:CClCO}_2\text{H} + \text{Br}_2 \rightarrow \text{PhCHBrCClBrCO}_2\text{H}$ , the addn. of Br to the  $\alpha$ -chlorocinnamic acids gives rise to products contg. 2 asymm. C atoms and hence capable of existing as 2 racemic mixts, whereas the addn. of Br to the  $\alpha$ -Br acids gives a product contg. only 1 asym. atom and capable therefore of existing in the form of 1 racemic mixt. Hence both the *cis*- and *trans*- $\alpha$ -bromocinnamic acids should yield the same dibromide, whereas the 2  $\alpha$ -Cl acids should yield 2 distinct racemic mixts. The same generalization should hold for the esters of the  $\alpha$ -chloro- and the  $\alpha$ -bromocinnamic acids, as well as for the corresponding  $\beta$ -chloro- and  $\beta$ -bromocinnamic acids and their esters. By the addn. of Cl to the  $\alpha$ -Cl and  $\alpha$ -Br acids the reverse should occur, i. e., both *cis*- and *trans*- $\alpha$ -Cl acids should give the same dichloride but distinct dibromides and similarly for the addn. of Cl to the  $\beta$ -Cl and  $\beta$ -Br acids. Relatively large amts. of the  $\alpha$ -bromocinnamic and  $\alpha$ -bromoalocinnamic acids were prepd. by the method of Sudborough and Thompson [*J. Chem. Soc.* 83, 666, 1155(1903)] and of the corresponding  $\beta$ -Br acids by the addn. of HBr to  $\text{PhC:CCO}_2\text{H}$ . The  $\alpha$ -Cl acids were prepd. from  $\text{PhCHClCHClCO}_2\text{H}$  by the action of NaOH [*J. Chem. Soc.* 89, 105(1906)] and the  $\beta$ -Cl by the addn. of HCl to  $\text{PhC:CCO}_2\text{H}$  (cf. James, C. A. 6, 504). The corresponding Me esters were prepd. by the Fischer-Speier method by using 5% HCl in MeOH. The yields were extremely good. Me  $\alpha$ -bromocinnamate, described by Beilstein as an oil, was obtained as a cryst. solid, m.  $22.5-23^\circ$ . Reactions were studied under the following conditions: (a) low temp.; (b) absence of light; (c) the addn. of the unsatd.

compd. to the halogen and not *vice versa*. A known vol. of pure Br in dry  $\text{CHCl}_3$  (0.5 g. Br per cc.) was run into a stoppered bottle cooled with ice, the theoretical amt. of acid or ester in  $\text{CHCl}_3$  was added in the dark and the mixt. kept for the required time (1 to 22 days). The contents were poured into a weighed dish, the  $\text{CHCl}_3$  and any excess Br allowed to evap. at ordinary temp., and the residue dried in a desiccator and weighed. Similar expts. were made except that the acid or ester soln. was added in ordinary daylight and the mixt. allowed to stand in daylight at ordinary temp. for the given time. Expts. made by exposing the finely divided  $\alpha$ -bromo and  $\alpha$ -bromoallo acid to the action of dry Br vapor in a desiccator in diffused daylight gave products identical with those obtained when  $\text{CHCl}_3$  solns. were used. The work shows that (1) the addn. of Br to the  $\alpha$ - and  $\beta$ -chloro- and -bromocinnamic acids in  $\text{CHCl}_3$  takes place much more readily in diffused daylight than in the dark. (2) The esters are more reactive than the free acids towards Br and the  $\beta$ -halogenated acids act on Br more readily than the isomeric  $\alpha$ -halogenated compds. (3) The following pairs of stereoisomerides give the same products: (a)  $\alpha$ -bromo- and  $\alpha$ -bromoalloeinnamic acid yield the same  $\alpha, \alpha, \beta$ -tribromo- $\beta$ -phenylpropionic acid, m.  $152-3^\circ$  (cor.). (b) Me  $\alpha$ -bromocinnamate and Me  $\alpha$ -bromoalloeinnamate both yield the same dibromide,  $\text{PhCHBr-CHBr-CO}_2\text{Me}$ , m.  $47-8^\circ$ . (c) The 2 stereoisomeric  $\beta$ -bromocinnamic acids yield the same  $\alpha, \beta, \beta$ -tribromo- $\beta$ -phenylpropionic acid, m. and decomp.  $146-7^\circ$ . (d) The Me  $\beta$ -bromocinnamate and stereoisomeric allo compd. both yield the same dibromide,  $\text{PhCHBr-CHBr-CO}_2\text{Me}$ , m.  $42-3^\circ$ . (e) The stereoisomeric  $\beta$ -chlorocinnamic acids yield the same dibromide, m. and decomp.  $143-4^\circ$ . (4) Each of the isomeric  $\alpha$ -Cl acids appears to yield a mixt. of 2 isomeric dibromides, which so far have not been sepd. E. H. VOEWILER

**The isomers and polymers of salicylides.** RICHARD ANSCHÜTZ. *J. prakt. Chem.* 105, 158-64(1922).—A study of the formation and the known reactions of  $\alpha$ -disalicylide (A)  $\beta$ -disalicylide (B), tetrasalicylide (C) and polysalicylide (D) in an attempt to ascertain their formulas. A. The m.-p. depression and the b.-p. elevation values indicate  $\text{C}_{14}\text{H}_8\text{O}_4$ . Its partial cleavage with MeOH, HOAc,  $\text{NH}_3$ ,  $\text{PhNH}_2$ ,  $p\text{-MeC}_6\text{H}_4\text{NH}_2$ , etc., to derivs. of  $o$ -salicylsalicylic acid and of  $o$ -diplosal and its formation from  $o$ -diplosal chloride indicate that it has the formula  $\text{C}_6\text{H}_4\text{CO.O.C}_6\text{H}_4\text{CO.O}$  (cf. C. A.

14, 1981). B. The m.-p. depression and b.-p. elevation indicate  $\text{C}_{14}\text{H}_8\text{O}_4$ . Its reaction

with  $\text{NH}_3$  indicates the formula  (cf. C. A. 14, 1981). C. The

formula proposed previously by A. (cf. *Ann.* 273, 100(1893)) is retained. D. No satisfactory formula is developed to explain its properties. C. C. DAVIS

**Phenylcoumarins.** D. C. CASTELL. *Mem. acad. cienc. art. Barcelona* 17, No. 10, 18 pp.(1922).—A new method of synthesis of  $\beta$ -phenylcoumarins consists in condensing HO derivs. of  $\text{Ph}_2\text{CH}_2$  with an ester of  $\text{Cl}_3\text{CHCO}_2\text{H}$ . 2,4,4'-Trihydroxybenzophenone reduced to  $(\text{HO})_2\text{C}_6\text{H}_3\text{CH}_2\text{C}_6\text{H}_4\text{OH}$  by the method of Clemmensen (Zn amalgam + HCl), the crude product mixed with an excess  $\text{Cl}_3\text{CHCO}_2\text{Et}$ , shaken with aq. NaOH, heated at  $100^\circ$ , acidified with HCl, filtered, and washed with  $\text{H}_2\text{O}$ , gave 4,4'-dihydroxy- $\beta$ -phenylcoumarin, needles from boiling EtOH, m.  $238-40^\circ$  (cf. C. A. 6, 2919). This procedure is recommended as a general method of prepn. of  $\beta$ -phenylcoumarins. An extensive survey of previous work on phenylcoumarins is included. C. C. DAVIS

**The bromination of camphene.** Dicumphenyl ether and a cyclo-homologous camphenylene. P. LIPP. *J. prakt. Chem.* 105, 50-64(1922).—A study of derivs. of camphene analogous to the work of Langlois (cf. C. A. 14, 2777).  $\omega$ -2-Dibromocamphene gave  $[\alpha]_D^{25} -24.72$  in 10% MeOH soln. It did not react with boiling  $\text{C}_3\text{H}_5\text{N}$  or  $\text{Ph-NMe}_2$ , but was decompd. by boiling quinoline.  $\omega$ -Bromocamphene (A), prepd. by the

method of Langlois, gave  $d_4^{25}$  1.285 and  $n_D^{25}$  1.52865. It did not react with PbO and H<sub>2</sub>O in a sealed tube at 220°, but was resinified by Ag<sub>2</sub>O and AgOH under similar conditions. *A* boiled with KOH, dild. with H<sub>2</sub>O, steam-distd. to remove a volatile by-product (see later), extd. with Et<sub>2</sub>O and fractionated, gave *dicamphenyl ether* (*B*), almost colorless oil with the consistency of glycerol,  $b_D$  182–6°, decompd. by heating with Na at ordinary pressure. Heated in xylene with Na with exclusion of air and evapd. *in vacuo*, it gave a liquid,  $b_D$  182°, with the odor of geraniums. In CHCl<sub>3</sub> 1 mol. adds 4 Br atoms with subsequent loss of 1 HBr. With aq. alk. KMnO<sub>4</sub> at 100° it gave no recoverable oxidation product. Heated at 100° in HOAc with CrO<sub>3</sub>, made alk. with K<sub>2</sub>CO<sub>3</sub> and steam-distd., it gave an unidentified ketone of the C<sub>10</sub> series. *B* with Pt black in abs. Et<sub>2</sub>O absorbed H<sub>2</sub> to give after fractionation a solid, m. 45–50°,  $b_D$  140°, consisting of a small % of an unidentified C:O compd. (with a semicarbazone, decomp. 236°) and a large % of an unidentified alc. Hydrolysis of *B* by H<sub>2</sub>SO<sub>4</sub> gave a mixt. of camphenylaldehyde and the 2 stereoisomeric camphenylanic acids (cf. *Ann.* 310, 122(1899)). The by-product obtained in the prepn. of *B* from *A* was transformed to its *semicarbazone* C<sub>11</sub>H<sub>19</sub>ON<sub>3</sub>, prisms from dil. EtOH, decomp. 235°. Steam-distd. in dil. H<sub>2</sub>SO<sub>4</sub> it gave *homocamphenylone* (cf. *C. A.* 14, 2914),

$$\text{OC} \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CMe}_2$$

a brittle solid of paraffin-like consistency, m.

38–40°,  $b_D$  85°, with an odor like camphenylone, but unlike the latter, decompd. in alk. emulsion at 100° by KMnO<sub>4</sub> to form after acidifying with H<sub>2</sub>SO<sub>4</sub> camphenecamphoric acid, crystals from hot H<sub>2</sub>O, m. 136–8°. This enlargement of a 5-ring to a 6-ring is analogous to that reported by Hintikka (cf. *C. A.* 8, 1583). C. C. D.

An attempt to prepare dihydrocampholytolactone by means of the Windaus degradation of glutaric acid. MARIA BREYER-SAVELSBERG. *J. prakt. Chem.* 105, 149–57 (1922).—Analogous to the degradation of aliphatic derivs. of glutaric acid by the method of Windaus (cf. *C. A.* 15, 2627), unsuccessful attempts were made to form dihydrocampholytolactone (*A*) from *cis*-camphoric acid (*B*). Aq. *B* treated with excess Ba(OH)<sub>2</sub>, then with CO<sub>2</sub> to remove the excess of Ba, next with AgNO<sub>3</sub> and EtOH, let stand in the dark, filtered, washed with EtOH and Et<sub>2</sub>O and dried *in vacuo*, gave *silver cis-camphorate* (*C*), fine powder, somewhat sol. in H<sub>2</sub>O, turned brown by light. *C* mixed with I and dry sand with exclusion of H<sub>2</sub>O, heated under pressure at 150°, extd. with Et<sub>2</sub>O, treated with NaHSO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, gave no *A* in the Et<sub>2</sub>O ext. The K<sub>2</sub>CO<sub>3</sub> layer, acidified and extd. with Et<sub>2</sub>O, gave *B*. The Ag salt of *o*-methyl camphorate (cf. Wien, *Monatsh.* 20, 685(1899)) mixed with I and sand with exclusion of H<sub>2</sub>O, heated under pressure at 150–60°, and sepd. as before into neutral and acid products, gave only *o*-methyl camphorate. C. C. DAVIS

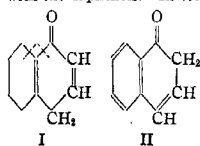
Some new components of camphor oil. F. ROCHUSSEN. *J. prakt. Chem.* 105, 120–36(1922).—New components of camphor oil were obtained from the phenol and the acid portions. By dissolving the mixt. of phenols in NaOH, adding CaCl<sub>2</sub>, filtering off the guaiacol homologs, washing with steam, decomp. by HCl, steam-distg. and fractionating, ethylguaiacol, 1,3,4-C<sub>6</sub>H<sub>3</sub>Et(OMe)OH, was isolated. The unidentified acid previously reported as C<sub>8</sub>H<sub>16</sub>O<sub>2</sub> by R. (cf. *Ber. Schimmel & Co.* Oct. 1922, 21) was isolated by converting the phenol-free fatty acids to their Et esters and fractionating and proved after extensive research, described in detail, to be inactive citronellonic acid (*A*). With this was isolated caproic (*B*) and caprylic acid (*C*). The relative quantities of *A*, *B* and *C* were approx. 22, 1 and 25, resp. C. C. DAVIS

Dyes derived from diphenic anhydride. SIKHIBHUSHAN DUTT. *J. Chem. Soc.* 123, 225–8(1923).—This work was undertaken with the idea that the condensation products, diphenins, might possess interesting tinctorial and fluorescent properties; while the fluorescent properties are only slightly less than those of the corresponding



Chemistry of naphthalene and its derivatives: chemical peculiarities of the naph-

**thalene nucleus.** N. N. VOROSHOV. *Bull. Inst. Poly. Ivanovo-Voznesensk* 6, 125-51 (1922).—A discussion of the 4 principal structural formulas which have been proposed for the  $C_{10}H_8$  mol.: (1) That proposed by Erlenmeyer (*Ann.* 137, 346(1866)) and Graebe (*Ber.* 1, 36(1868)) and expounded by Marckwald [*Ann.* 279, 1-23; *Ber.* 28, 114-6(1895)] and composed of 2 benzene rings having 2 common C atoms; (2) Bamberger's formula (*Ann.* 257, 1-55); (3) Thiele's formula (*Ann.* 306, 87-142(1899)), and (4) the formula proposed by Harries (*Ann.* 343, 311-75(1905)) and Willstätter and King (*C. A.* 7, 1508). The identity of the 2 six-membered rings in  $C_{10}H_8$  appears certain, in the absence of evidence that isomeric mono-substituted naphthalenes exist with the substituents in the same position. Besides being unsym., Willstätter's formula rests on inadequate foundations. Thiele's formula appears the most probable, as it brings out the special reactivity of the  $\alpha$ -position. The different behavior shown towards reagents by  $C_8H_8$  and by octatetrene cannot be advanced as an argument against Thiele's theory, as it may be explained by differences between 6- and 8-membered rings. In the mono-HO- and -NH<sub>2</sub> derivs. of  $C_{10}H_8$ , however, the  $C_{10}H_8$  nucleus exhibits other relations. The results of V.'s investigations on the action of NaHSO<sub>3</sub> on  $C_{10}H_8$  derivs. (*C. A.* 10, 2896) do not agree with Bucherer's statements (*J. Prakt. Chem.* [ii] 69, 49-91(1904); 70, 345-64(1905)), and show that the naphthols are not esterified by H<sub>2</sub>SO<sub>3</sub> or sulfites, but first yield additive compds. which are regarded as formed from the ketones isomeric with the naphthols. In view of the marked analogy in reaction relationships between



the H atom in the 4-position of  $\alpha$ -naphthol and that in the 1-position of  $\beta$ -naphthol, the constitution I is favored for the keto-form of  $\alpha$ -naphthol, although the structure II is not excluded. Thiele's theory of conjugated double linkings renders it probable that the keto-forms of the naphthols are but slightly unsatd. The divergent behavior shown by  $C_8H_8$  and  $C_{10}H_8$  derivs. evidenced in the alkylation of the naphthols in acid soln., in the amination of the IIO group and hydrolysis of the NH<sub>2</sub> group, and in the reaction with sulfites, is readily explainable on the assumption that the HO and NH<sub>2</sub> derivs. of the  $C_{10}H_8$  series more readily undergo ketoenolic transformations than the corresponding compds. of the  $C_8H_8$  series. Thus, IIO derivs. of  $C_{10}H_8$  are true enols, whereas the HO of the mono-HO derivs. of the  $C_8H_8$  series functions as aromatically combined IIO; this conclusion is not in accord with the views of Meyer (*C. A.* 7, 2539) but is supported by various reactions of  $C_{10}H_8$  derivs. Application of the sulfite reaction to the 1,5- and 1,8- $C_{10}H_7(NH_2)$  results in the formation of the additive compd. first in one of the substituted rings, the 2nd ring remaining intact as a typically aromatic ring. If then the H<sub>2</sub>SO<sub>3</sub> additive compd. is destroyed, the NH<sub>2</sub> group of the 2nd ring reacts on subsequent treatment with H<sub>2</sub>SO<sub>4</sub>; in this case the 2nd ring exhibits aliphatically unsatd. and the 1st aromatic behavior. The various stages of the reaction are in agreement with V.'s views.

J. C. S.

**The chemistry of anthraquinone.** EUG. GRANDMOUGIN. *Chimie et industrie* 7, 627-33, 879-85; 8, 47-56(1922); 9, 46-52(1923).—A review. A. P.-C.

**The catalytic action of mercury in the sulfonation of anthraquinone.** G. W. CLOUGH. *J. Soc. Dyers Colourists* 38, 290-300(1922).—Further investigation is recommended of the explanation of Roux and Martinet (*C. A.* 15, 1497, 2640) in regard to the formation of anthraquinone- $\alpha$ -sulfonic acid by sulfonation in the presence of Hg. C. was unable to verify their expts. in converting the Na anthraquinone- $\alpha$ -sulfonate into the  $\beta$ -sulfonate by heating with H<sub>2</sub>SO<sub>4</sub> at 180°; or producing the  $\beta$ -sulfonate by sulfonation of anthraquinone in the presence of Hg at 160°. CHAS. E. MULLIN

**Arylamine salts of the anthraquinonesulfonic acids.** A. G. PERKIN AND W. G.

SEWELL. *J. Soc. Chem. Ind.* **42**, 27-31T(1923).—By adding the  $\text{NH}_2$  compd., in an excess of dil.  $\text{HCl}$ , to the Na salts of the sulfonic acids in boiling  $\text{H}_2\text{O}$ , the following arylamine salts were prepd.: with anthraquinone- $\beta$ -monosulfonic acid: aniline, needles, m.  $309^\circ$ , sol. in 1700 parts  $\text{H}_2\text{O}$ ; *p*-toluidine, needles, m.  $308^\circ$ , sol. in 2500 parts  $\text{H}_2\text{O}$ ;  $\alpha$ -naphthylamine, m.  $253^\circ$ ; monomethyl aniline, fine needles, m.  $202-3^\circ$ , sol. in 310 parts  $\text{H}_2\text{O}$ ; dimethylaniline, m.  $192-4^\circ$ , sol. in 71 parts  $\text{H}_2\text{O}$ ; diethylaniline, m.  $174-5^\circ$ ; quinoline, plates from alc., m.  $225^\circ$ ; pyridine, plates from alc.; with anthraquinone- $\alpha$ -sulfonic acid: aniline, needles, m.  $281^\circ$ ; monomethylaniline, m.  $213^\circ$ ; dimethylaniline, m.  $215.5^\circ$ ; quinoline, needles from alc., m.  $195^\circ$ ; pyridine, needles from alc., m.  $158^\circ$ ; with 1,5-anthraquinonedisulfonic acid: aniline, orange-yellow crystals, contg.  $3\text{H}_2\text{O}$ ; monomethylaniline, orange-yellow plates with  $3\text{H}_2\text{O}$ , m.  $251^\circ$ , which lose  $\text{H}_2\text{O}$  at  $100^\circ$  and m.  $255^\circ$ ; dimethylaniline, crystals from  $\text{H}_2\text{O}$ ; with 1,8-anthraquinonedisulfonic acid: aniline, needles from alc.; monomethylaniline, small crystals from alc.; dimethylaniline, plates from alc., m.  $278^\circ$ ; with 2,6-anthraquinonedisulfonic acid: aniline, plates from alc.; monomethylaniline, needles from alc., m.  $205-10^\circ$ ; dimethylaniline, large needles from alc.; with 2,7-anthraquinonedisulfonic acid: aniline, plates from  $\text{H}_2\text{O}$ ; monomethylaniline, needles from alc., m.  $230^\circ$ ; dimethylaniline, needles from alc. The low soly. of the  $\text{PhNH}_2$  salt permits its use in the analysis of anthraquinonesulfonic acid. The salt is pptd., filtered off, suspended in boiling  $\text{H}_2\text{O}$ , and titrated with 0.1 *N* alkali, with phenolphthalein. The difference in soly. between the mono- and dimethylaniline salts permits a partial sepn. of these bases.

T. S. CARSWELL

peri-Naphthindigotin. SIKHIBHUSHAN DUTT. *J. Chem. Soc.* **123**, 224-5(1923).—peri-Naphthindigotin was obtained as a dark blue cryst. aggregate by heating a mixt. of  $\text{NaO}_2\text{CC}_{10}\text{H}_6\text{NCH}_2\text{CO}_2\text{Na}$  (Fierz and Sallmann, *C. A.* **16**, 3898),  $\text{NaOH}$  and  $\text{NaNH}_2$  at  $280^\circ$  until frothing ceased and then at  $300^\circ$ . Alk.  $\text{Na}_2\text{S}_2\text{O}_4$  gives a reddish brown soln. which dyes wool and cotton light green shades which are rather fugitive to light. The soln. in concd.  $\text{H}_2\text{SO}_4$  is bluish green; when rubbed between hard surfaces the compd. acquires a Cu-colored metallic luster.

C. J. WESSER

N-Substituted oxindoles and isatins. R. STOLLÉ. *J. prakt. Chem.* **105**, 137-48 (1922).—A resumé of the theoretical aspects of the prepn. of compds. already published separately (cf. Bergdoll, "Über die Darstellung von Oxindol und Oxindolabkömmlingen," *Diss. Heidelberg* 1920; Luther, "Über die Einwirkung von Oxalylchlorid auf N-substituierte Aniline," *Diss. Heidelberg* 1920; Auerhahn, "Über stickstoffsubstituierte Isatine," *Diss. Heidelberg* 1921; Wacker, "Über Abkömmlinge des Phenylloxindols und des Äthylloxindols," *Diss. Heidelberg* 1921). The actual prepn. and properties of the compds. are to be published collectively soon.

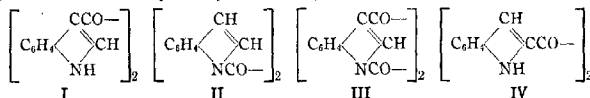
C. C. DAVIS

The constitution of naphtholisatin and its derivatives. C. CÂNDREA. *Bull. sec. sci. acad. Roumaine* **8**, 31-9(1922-3).—C. briefly reviews (with numerous references) previous work on the constitution of isatin (*A*), and describes the prepn. of condensation products of *A* with  $\alpha$ -naphthol (*B*). Di- $\alpha$ -naphtholisatin,  $\text{C}_{28}\text{H}_{19}\text{O}_2\text{N}$ . Heat 1 g. of *A* in 10 g. of *B*, add 5-6 drops of  $\text{H}_2\text{SO}_4$ , and remove excess of *B* with hot water. The residue of blue crystals insol. in alc.,  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$ , and benzene, difficultly sol. in  $\text{Me}_2\text{CO}$ , can be obtained as prismatic crystals, m. above  $300^\circ$ , from  $\text{Me}_2\text{CO}$  by careful addn. of  $\text{H}_2\text{O}$ , and from glacial  $\text{AcOH}$ . Di- $\alpha$ -naphtholmonobromoisatin,  $\text{C}_{28}\text{H}_{19}\text{O}_2\text{NBr}$ , obtained in the same way from monobromoisatin, crysts. from  $\text{Me}_2\text{CO-H}_2\text{O}$  as prismatic needles, insol. in alkalis, m. above  $300^\circ$ . Di- $\alpha$ -naphtholdibromoisatin,  $\text{C}_{28}\text{H}_{17}\text{Br}_2\text{O}_2\text{N}$ , from dibromoisatin, insol. in alc.,  $\text{Et}_2\text{O}$ ,  $\text{EtOAc}$ , alkalis,  $\text{H}_2\text{SO}_4$ , difficultly sol. in  $\text{Me}_2\text{CO}$ , almost insol. in  $\text{CHCl}_3$  and benzene, sol. in hot  $\text{PhNO}_2$ , crysts. from  $\text{PhNO}_2$ -alc. as prismatic needles, m. above  $300^\circ$ . Di- $\alpha$ -naphtholmonochloroisatin,  $\text{C}_{28}\text{H}_{19}\text{O}_2\text{NCl}$ , insol. in alkalis, m. above  $300^\circ$ . Di- $\alpha$ -naphtholdichloroisatin,  $\text{C}_{28}\text{H}_{17}\text{O}_2\text{NCl}_2$ , prismatic needles, insol. in alc.;  $\text{Et}_2\text{O}$ , difficultly sol. in  $\text{CHCl}_3$ , glacial  $\text{AcOH}$ ,  $\text{Me}_2\text{CO}$ , very difficultly sol. in

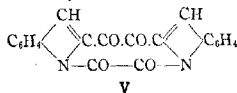
AcOEt, almost insol. in benzine, gasoline, can be recrystd. from  $\text{CHCl}_3$ -gasoline, m. above  $300^\circ$ .

A. P.-C.

**$\alpha$ -Diketones of the indole group. I.** G. SANNA. *Gazz. chim. ital.* **52**, II, 165-70 (1922).—In a previous paper Oddo and S. (*C. A.* **16**, 1423) obtained compds. by the action of  $(\text{COCl})_2$  on magnesiylindole (*A*), of which  $\beta,\beta$ -diindoyl (I), *N,N*-diindoyl (II), and a *N,C*-deriv. (III) were described. S. now describes 3 other products obtained under conditions not yet fully established, which will be described later. The

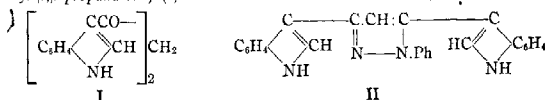


$\text{PhNHNH}_2$  and  $o\text{-C}_6\text{H}_4(\text{NH}_2)_2$  derivs. are also described. I in dil. AcOH soln. heated with 3 mols.  $\text{PhNHNH}_2 \cdot \text{HOAc}$ , sepd. the  $\beta,\beta$ -diindoyl osazone (*B*) of I, yellow prisms, m.  $158^\circ$ . *B* in EtOH with  $\text{FeCl}_3$  is visibly oxidized (red color) to the corresponding osotetrazone. The AcOH soln. of I heated with 1 mol.  $\text{C}_6\text{H}_4(\text{NH}_2)_2 \cdot \text{HCl}$  sepd. on cooling and dilg.  $\beta,\beta$ -diindoylquinoxaline, red prisms, m.  $163^\circ$  (decompn.). In order to confirm the attachment of the 2 CO groups to C the silver salt of I,  $\text{C}_{18}\text{H}_{14}\text{O}_2\text{N}_2\text{Ag}_2$ , was prepd. as a grayish ppt. by adding  $\text{AgNO}_3$  soln. + some drops of  $\text{NH}_4\text{OH}$  to the EtOH- $\text{H}_2\text{O}$  soln. of I. With  $\text{H}_2\text{O}_2$  I gave  $\beta$ -indolecarboxylic acid, m.  $212\text{--}3^\circ$ , thus proving that the 2 CO groups are attached to C in the  $\beta$ -position. If the products of reaction with  $(\text{COCl})_2$  are carefully fractionated  $\alpha,\alpha$ -diindoyl (*2,2*-indil (IV)) seps. in the less sol. fractions as yellow tabular prisms, m.  $273^\circ$ .  $\alpha,\alpha$ -Diindoyl osazone was obtained as with I as yellow prisms, m.  $170^\circ$  (decompn.), oxidized to the red Et<sub>2</sub>O-sol. osotetrazone with  $\text{FeCl}_3$ .  $\alpha,\alpha$ -Diindoylquinoxaline was obtained from IV as with I as red needles, m.  $154^\circ$  (decompn.). IV with 30%  $\text{H}_2\text{O}_2$  and extn. with Et<sub>2</sub>O gave  $\alpha$ -indolecarboxylic acid (*C*), m.  $200^\circ$ . Fusing IV with KOH also gives *C*, which confirms the constitution of IV. Of the products of reaction of *A* with  $(\text{COCl})_2$  all are easily sol. in EtOH except 1 product that is only sol. in boiling abs. EtOH. This is *bis*-1,2-indil (*bis*-*N,N*- $\alpha$ -diindoyl (V), yellow scales, m.  $320^\circ$ . V heated with concd. KOH, cooled, acidified with dil.  $\text{H}_2\text{SO}_4$  and extd. with Et<sub>2</sub>O gave IV, m.  $273^\circ$ . If fused with KOH V gives *C*. That the *N*-position is occupied is indicated by the fact that it gives no ppt. with  $\text{AgNO}_3 + \text{NH}_4\text{OH}$ . Another undetd. product that m.  $163^\circ$  was sepd. in very small amts.



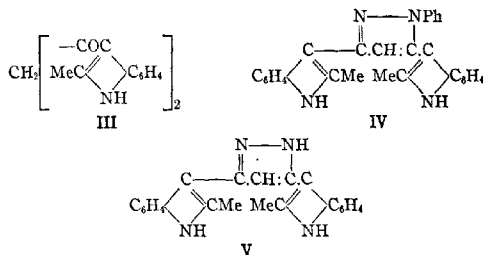
E. J. WITZEMANN

**Synthesis of  $\beta$ -diketones in the indole group. I, II.** G. SANNA. *Gazz. chim. ital.* **52**, II, 170-6, 177-84 (1922).—In extending previous work by Oddo and S. (*C. A.* **16**, 1423) S. has studied the action of malonyl chloride (*A*) on indole magnesium bromide. Oddo (*C. A.* **5**, 2638) obtained from *A* and *B* a pyrrolic  $\beta$ -diketone having the side chain bound to the  $\alpha$ -C atom. S. has now obtained diindoylmethane ( $\beta,\beta$ -diindyl- $\beta,\beta$ -propandione) (I) with the side chain bound to the  $\beta$ -C atom. I is slowly



sol. in alkalis and is repptd. unchanged by dil.  $\text{H}_2\text{SO}_4$ . With  $\text{AgNO}_3$  and some  $\text{NH}_4\text{OH}$  the silver salt of I is pptd. by substituting the H atoms in the 2 NH groups. \*When

boiled with alkalis **I** gives  $\beta$ -indolecarboxylic acid and  $\beta$ -indole Me ketone. **I** reacts easily with  $\text{PhNHNH}_2$ , giving a dehydration product of the monophenylhydrazine, i. e., 1-phenyl-3,5-diindylpyrazole (**II**), as was demonstrated by converting it into the corresponding pyrazoline (**C**). By a similar mechanism **I** with  $\text{NH}_2\text{OH}$  gave 3,5-diindylisoxazole (**D**). With  $\text{NH}_2\text{CONHNH}_2$  **I** gives 3,5-diindylpyrazolecarboxamide (**E**), which on adding  $\text{H}_2\text{O}$  loses  $\text{CO}_2$  and  $\text{NH}_3$ , giving 3,5-diindylpyrazole (**F**). The reactions of **I** are those of the enol form but its behavior with Cu salts,  $\text{FeCl}_3$ , and alkalis suggest that most of it exists in the keto form. The 2 tautomeric forms were not sep'd. Other isomers of **I** could not be found, which suggests that the length of the chain influences the tendency to attack in a position farther from the NH group. 2 mols. **B** in dry  $\text{Et}_2\text{O}$  were treated slowly with **A** in  $\text{Et}_2\text{O}$  and after 12 hrs. with ice.  $\text{Et}_2\text{O}$  was removed by warming. The ppt. was filtered off and boiled with a little  $\text{EtOH}$  to remove unchanged indole. The residue crystd. from much  $\text{EtOH}$  gave **I** as crystals, blacken  $230^\circ$  but do not m. even at  $287^\circ$ .  $\text{EtOH}$  solns. of **I** +  $\text{PhNHNH}_2\cdot\text{HCl}$  were boiled 48 hrs. and gave **II** as yellow prisms, m.  $236^\circ$  (decompn.), which reduced in boiling  $\text{EtOH}$  with Na gave **C**. **I** boiled in  $\text{EtOH}$  48 hrs. with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  +  $\text{Na}_2\text{CO}_3$  gave **D** as yellow prisms, m.  $219^\circ$ . On heating **I** with  $\text{NH}_2\text{CONHNH}_2$  +  $\text{NaOAc}$  for a few days **F** seps., yellow crystals, m.  $229^\circ$  (decompn.). Dimethylketolmethane ( $\beta,\beta$ -dimethylketol- $\gamma,\gamma$ -propanedione) (**III**) obtained from **A** and methylketolmagnesium bromide by the method used with the indole deriv., resembles its lower homolog in its chem. properties. Boiled with alkali it decomps. giving  $\alpha$ -methyl- $\beta$ -indolecarboxylic acid and



$\alpha$ -methyl- $\beta$ -indolyl Me ketone. With **III**  $\text{PhNHNH}_2$  gives 1-phenyl-3,5-dimethylketylpyrazole (**IV**) as slightly yellow prisms, m.  $192^\circ$  (decompn.), which on reduction gives the corresponding pyrazoline. With  $\text{NH}_2\text{OH}$  **III** gives 3,5-dimethylketylpyrazole as yellowish prisms, m.  $174^\circ$  (decompn.). With  $\text{NH}_2\text{CONHNH}_2$  **III** gives 3,5-dimethylketylpyrazole (**V**) by loss of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{NH}_3$  from the semicarbazide. Besides **III**, which behaves like the hydroxy ketone  $-\text{C}\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{CO}-$ , S. isolated another form having the same m. p. but a different cryst. form, which, unlike **III**, is insol. in alkalis, gives no color with  $\text{FeCl}_3$  nor a ppt. with  $\text{Cu}(\text{OAc})_2$  but gives **IV** and **V**, etc., with  $\text{PhNHNH}_2$ ,  $\text{NH}_2\text{OH}$  and  $\text{NH}_2\text{CONHNH}_2$ . This is considered to be the normal form of **III** ( $-\text{CO}\cdot\text{CH}_2\cdot\text{CO}-$ ) and will be discussed in detail in a later paper. Another product that appears to be **III** minus 1 mol.  $\text{H}_2\text{O}$  was obtained, is partly described and is being studied further for a fuller report. **III** was obtained as yellow rhombohedral tablets, m.  $219^\circ$ , from  $\text{EtOH}$  when the original product was extd. with  $\text{Et}_2\text{O}$ . The larger part of the product is insol. in  $\text{Et}_2\text{O}$  but dissolves easily in  $\text{EtOH}$ , from which it seps. as yellow microcrystals, m.  $219^\circ$ . Of these the former is the more chemically inert form of **III**.

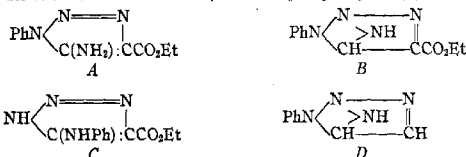
E. J. WITZEMANN

**Tautomerism of amidines. I. 2,4- and 2,5-Diphenylglyoxalines.** RICHARD BURTLES AND F. L. PYMAN. *J. Chem. Soc.* 123, 361-7(1923).—Thus far there is but

one uncontradicted example of isomerism among the amidines, the occurrence of 2,4-diphenylglyoxaline (*A*) (Minovici, *Ber.* 29, 2097) and the 2,5-deriv. (*B*) (Kunckell, *Ber.* 34, 637). The formation of these 2 bases has been confirmed. They yield identical salts with any given acid, from which the recovered base is *A*. Hydrochloride, m. 274°. Hydrogen oxalate, m. 225°. Acetate, m. 95°. *B* is transformed into *A* by heating a short time in EtOH. In no case has the reverse change been carried out. Satd. alc. solns. of the more sol. base *A* failed to deposit the less sol. base *B*. The following soly. in g. per 100 g. abs. EtOH are reported for *A*, *B*, and *A* + *B*: 0°, 11.3, 3.5, 10.6; 10°, 14.8, 4.4, 14.9; 25°, 16, —, 18.5; 27°, —, 5.9, —; 36°, 23.6, —, 23.3. In the region of the m. p. the stable compd. is *A*. A mixt. of *A* and *B* m. 174–5°, intermediate between their m. p. These facts indicate that the compds. are isomeric and not polymorphic but it is not possible to judge from their method of formation which is the 2,4- and which the 2,5-isomer. II. The alkylation of open-chain amidines. F. L. PYMAN, *Ibid* 367–70.—In the action of MeI upon CPh(:NPh)NIMe (or CPh(:NMe)NHPh), contrary to earlier results, the 2 isomers CPh(:NMe)NMePh and CPh(:NPh)NMe<sub>2</sub> are formed in the ratio of 15:1. These and earlier results (*C. A.* 17, 561) lead to the conclusion that the alkylation of open-chain, as well as cyclic amidines, gives a mixt. of the 2 isomeric alkyl derivs. in proportions which depend upon the relative character of R and R', the greater the difference between R and R', the greater being the difference in the yield of the 2 isomers.

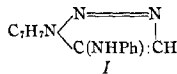
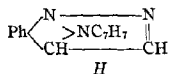
C. J. WEST

**2,5-Iminodihydro-1,2,3-triazole.** I. Constitution of Dimroth's 5-anilino-1,2,3-triazole. P. K. DURR, *J. Chem. Soc.* 123, 265–74 (1923).—In order to decide between *A* and *B* as the formula for 5-anilino-1-methyltriazole (Dimroth, *C. A.* 3, 1170), 2 different series of compds. have been made under exactly similar conditions. Et 5-amino-1-phenyl-1,2,3-triazole-4-carboxylate (*A*), by the interaction of phenylazoimide and CN·CH<sub>2</sub>CO<sub>2</sub>Et in EtONa, m. 125–6°. The free acid m. 140°. Acetate, m. 103–4° (D. gives 90°). In dry C<sub>6</sub>H<sub>5</sub>N this gives ethyl 2,5-imino-1-phenyldihydro-1,2,3-triazole-4-carboxylate (*B*), m. 124–6° (D. formulated this as *C*); the Ac deriv. is the same as that of *A*. The methyl deriv. is formed by boiling *B* with MeI and EtONa, m. 98–9°. Hydrolysis gives the free acid, C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>N<sub>4</sub>, m. 222°. *B* is converted into *A* by heating with EtOH into which dry HCl is passed for 6–7 hrs. Hydrolysis of the Ac deriv. with EtOH and dry HCl gives some *A* and a considerable quantity of *B*, and the Ac compd. is therefore derived from the latter. 2,5-Imino-1-phenyldihydro-1,2,3-triazole (*D*)



(*Ber.* 35, 4041) is best prepd. by heating the free acid from *A* with dry C<sub>6</sub>H<sub>5</sub>N at 120–30° for 2 hrs.; picrate, m. 163° (decompn.). Acetate, m. 141–1.5°. Methyl deriv., m. 198–9°. The nitroso deriv. of *B* m. 117–8°. The alk. soln. is colorless but turns red when warmed. After standing in the light for some time, it turns greenish yellow and then gives red alk. solns. Recrystd. from EtOH, it is again colorless. Heated in NaHCO<sub>3</sub> partial decompn. occurs, and upon addn. of acid, *B* is recovered. Likewise the action of PhNH<sub>2</sub> gives *B*, together with H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NhPh. Ethyl 5-hydroxy-1-phenyl-1,2,3-triazole-4-carboxylate (*E*), yellow, m. 72–3°. The 1-*p*-tolyl deriv. is dull yellow and m. 98–9°. Ethyl 5-chloro-1-phenyl-1,2,3-triazole-4-carboxylate (*F*), from *E* and PCl<sub>5</sub>, m. 80–1°. 1-*p*-Tolyl deriv. (*G*) m. 61–2°. The action of *p*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> on *F*, followed by hydrolysis and warming in EtOH on the H<sub>2</sub>O bath, gives 2,5-*p*-tolylimino-

1-phenyldihydro-1,2,3-triazole (H), m. 171-2°, also obtained by the action of  $\text{PhNH}_2$  on G. It does not form an acetate nor does it give a N-NO deriv. and therefore its con-



stitution must be represented by H and not I.

C. J. WEST

Addition of hydrazoic acid to adjacent double bonds. VIII. 1-Phenyl-5-anilino-tetrazole and dithiocarbamic acid azide. E. OLIVIERI-MANDALÀ. *Gazz. chim. ital.* **52**, II, 139-44(1922).—In preceding papers O.-M. (*C. A.* **7**, 3755) has discussed the easy addn. of  $\text{HN}_3$  to compds. contg. adjacent double bonds. Instead of adding thus,  $-\text{NH.N:N}-$ , as with  $\text{CH}_2\text{N}_2$ , which gives  $-\text{NH.N:CH}-$ , the reaction takes place in 2 stages thus:  $\text{RN:C:NR} + \text{HN}_3 \longrightarrow \text{RN:C(N)} - \text{NHR} \longrightarrow \text{RN.N:N.N:CNHR}$ .

$\text{C}(\text{NPh})_2$  (Weith, *Ber.* **7**, 10(1874)) was obtained by the action of  $\text{HgO}$  on  $\text{CS}(\text{NHPh})_2$  in  $\text{C}_6\text{H}_6$ . The filtered cold soln. was treated with excess  $\text{HN}_3$  in  $\text{Et}_2\text{O}$ . Overnight 1-phenyl-5-anilino-tetrazole (A) sepd. as needles, m. 162°. With  $\text{Ac}_2\text{O} + \text{NaOAc}$  A gives an acetyl deriv.  $\text{C}_{16}\text{H}_{13}\text{N}_5\text{O}$ . A is indifferent to bases and acids but in  $\text{EtOH}$  ppts. a silver salt with  $\text{AgNO}_3$ . A is identical with the phenyliminophenyltetrazolone of Busch and Bauer (*Ber.* **35**, 1058(1900)) but O.-M. considers it to be a deriv. of 1,2,3,4-tetrazole [pyrro-( $\alpha,\beta,\beta'$ )-triazole] which in the formation of salts isomerizes thus:  $\text{RN.N:N.N:CNHR} \longrightarrow \text{RN.N:N.NH.C:NR}$ . A at the m.p. decomps., giving

N-phenylpyrro- $\alpha,\beta,\beta'$ -triazole,  $\text{RN.N:N.N:CH}$ , m. 65°.  $\text{HN}_3$  also adds to  $\text{CS}_2$  in  $\text{Et}_2\text{O}$ ,

giving  $\text{S:C(N)}\text{SH}$  (B) and then  $\text{S.N:N.N.CSH}$  or  $\text{S.N:N.NH.C:S}$ . The behavior

of the product corresponds to that of B, i. e., of azides of thiocarbamic acids:  $\text{B} - \text{N}_2 \longrightarrow \text{S.C(SH):N-S} \longrightarrow \text{HSC:N} + 3\text{HCNS} \longrightarrow \text{HCN} + \text{H}_2\text{C}_2\text{N}_2\text{S}_3$ . B in  $\text{EtOH}$  ppts.

$\text{CS}_2\text{N}_3\text{Na}$  on adding  $\text{NaOH-EtOH}$  (cf. also Sommer, *C. A.* **10**, 342). In summarizing all this work O.-M. found that  $=\text{C:NR}$ ,  $\text{O:C:CR}_2$ ,  $\text{O:C:NR}$ ,  $\text{S:C:NR}$ ,  $\text{R.N:C:NR}$ , and  $\text{S:C:S}$  all add  $\text{HN}_3$  easily in such a way that the  $\text{N}_3$  group adds to the C atom and the H atom to N. Moreover the unsatd. groups  $-\text{N:CN}_2$  and  $=\text{C:CN}_2$  isomerize rapidly giving  $\text{C.N.N.N.N}$  and  $\text{C.C.N.N.N}$ , resp.  $\text{C}(\text{NPh})_2$  reacts more easily with  $\text{HN}_3$

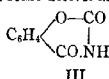
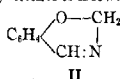
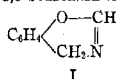
than  $\text{PhN:C:O}$ , which agrees with observations of Staudinger and Meyer (*C. A.* **14**, 2490) that substitution of CO with C:NPh increases reactivity. E. J. WITZEMANN

Some derivatives of methylenediquinaldine and their relationship to the carbocyanines. FRANCES M. HAMER. *J. Chem. Soc.* **123**, 246-50(1923).—This work was undertaken with the idea of proving the formula for pinacyanol suggested in *C. A.* **15**, 829, starting with methylenediquinaldine dialkyl halide. It was found that the interaction of 1 mol. 40%  $\text{HCHO}$  and 2.5 mols.  $\text{MeC}_6\text{H}_4\text{N.MeI}$  in the presence of  $\text{EtOH}$  and a little  $\text{C}_6\text{H}_{11}\text{N}$  gave an 80% yield of methylenediquinaldine dithiodide (A), deep orange, m. 210° (decompn.), stable to boiling  $\text{H}_2\text{O}$ . Dimethochloride, very hygroscopic, m. 184-6° to a blue liquid with decompn. Dimethobromide, contg. 1 mol.  $\text{H}_2\text{O}$  (lost in *vacuo* at 80-90°), m. 180-5°. Dimethonitrate, pink, decomps. 120° and becomes quite black at the m. p., 178-80°. It is stable towards oxidizing agents (dil.  $\text{HNO}_3$ ). Diethiodide, obtained in 46% yield through the  $\text{EtCl}$  deriv., which was not isolated, yellow, m. 204-7°. 6,6'-Dimethylenediquinaldine diethiodide (B), (yield, 33%), pale yellow with 1  $\text{H}_2\text{O}$  when dried over  $\text{H}_2\text{SO}_4$ , or anhyd. when heated in *vacuo* at 80-90°. The action of alkalis in the cold did not effect the removal of halogen acid to any extent. while on heating a small amt. of carbocyanine was produced. A 42% yield of 1,1'-

dimethylcarbocyanine iodide (*C*) was obtained by the action of 3.5 mols. Na upon 1 mol. *A* and 2 mols.  $C_6H_7N.MeI$  in hot  $EtOH$  contg. 0.5 mol.  $HCl$ . Using 1 mol. each, the optimum yield was obtained with 2.5 mols. Na. The yield of the  $1,1'-Et_2$  deriv. was 47%. Since *C* was obtained in 38% yield by the use of *A* and 6-Me $C_6H_4N.EtI$ , it is shown that the quaternary compd. plays no direct part in the production of *C*. This was further confirmed by the action of Na upon *B* and  $C_6H_7N.MeI$ , the product being 6,6'-dimethyl-1,1'-diethylcarbocyanine iodide (38% yield). Thus the part acted by the quinolinium salt in this condensation is still obscure. Benzylidenediquinaldine (Koenigs, *Ber.* 32, 3599) was obtained as the hydrochloride, m.  $154-6^\circ$  in 55% yield; the free base, m.  $90-4^\circ$ , is transformed into a higher m. form at  $100^\circ$ , and then m.  $106.5-7.5^\circ$ . The reverse transformation was accomplished by soln. in  $Et_2O$ . Both forms give the same  $HCl$  and  $MeI$  derivs. *Dinitrate*, pale yellow, m.  $100-12^\circ$ . *Dimethiodide* (*D*), very pale yellow, m.  $183-200^\circ$  (decompn.). At a lower temp. ( $48^\circ$ ), the *monomethiodide*, m.  $170-7^\circ$ , resulted. Boiling with  $H_2O$  changes *D* into *benzylidenequinaldine methiodide*, orange, m.  $231-2^\circ$ . Alkali brought about a complete disruption of the mol. of both derivs.

C. J. WKEST

**1,3-Benzoxazines.** Passage from isonitrosocoumaranones to derivatives of 1,3-benzoxazine. I. EFISIO MAMELI. *Gazz. chim. ital.* 52, II, 184-9(1922).—Of the 2 possible 1,3-benzoxazines (I and II) neither is known, although some derivs. are known,



including 2,4-diketo-1,3-benzisoxazine (III). M. obtained 5-methyl-8-isopropyl-2,4-diketo-1,3-benzisoxazine (*A*) by transposition with  $PCl_5$  of 4-methyl-7-isopropyl-2-isonitrosocoumaranone (*B*), prepd. (*C. A.* 16, 2688) by the action of  $HNO_3$  on 4-methyl-7-isopropyl-3-coumaranone (*C*), obtained in turn from the thymoxyacetic acid. After briefly reviewing the Beckmann rearrangement M. points out that this is the 1st instance of the transposition of the pentagonal furanic ring (such as that of *B*) into a hexagonal ring (such as the oxazinic ring of *A*). The constitution of *A* was established by its method of formation and by its conversion into 6,2,3-Me(HO)( $C_6H_4$ )- $C_6H_5CONH_2$  (*D*), which was also synthesized from thymotic acid. M. expects to det. if the formation of *A* is a general reaction. To 3 g.  $PCl_5$  suspended in petroleum ether 3 g. *B* were added in an app. with a reflux condenser sealed with a  $H_2SO_4$  valve. The mixt. evolved  $HCl$  on warming. After 3 hrs. the solvent was evapd. The residue was treated with  $H_2O$  ( $HCl$  evolved) and recrystd. from  $EtOH$ . *A* sepd. as fine white needles, m.  $152-3^\circ$ , decomp.  $177^\circ$ , sol. in alkalis and alk. carbonates but pptd. unchanged by acids, remains unchanged when boiled with dil.  $HCl$  but when boiled with alkalis gives *D*. *A* in the calcd. amt. of  $KOH.EtOH$  gives the *potassium salt* as a powder on evapn. The *silver salt* is pptd. by double decompn. of the K salt. The K salt heated with  $MeI + abs. MeOH$  at  $150^\circ$  for 4 hrs. in a sealed tube sepd. the *methyl ester* of *A* as needles, m.  $129^\circ$ . The *ethyl ester* was obtained similarly as a cryst. powder, m.  $104^\circ$ . *A* boiled 30 mins. with 7%  $NaOH$  gave with acids a ppt. of *D*, needles from  $EtOH$ , m.  $137^\circ$ , decomp.  $205^\circ$ . *Et* thymotate in alc. satd. with dry  $NH_3$  at  $0^\circ$  and heated 8 hrs. at  $130^\circ$  gave a *D* identical with the above prepn.

E. J. WITZEMANN

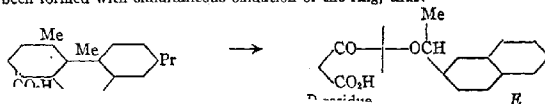
The spectrochemistry of derivatives of tropane. K. VON AUWERS. *J. prakt. Chem.* 105, 102-19(1922).—Extensive data are given of the optical properties of the following compds.: tropane, tropidine, tropine, acetyl tropine, propionyl tropine, tropinone, *Et* tropane-2-carboxylate, *Et* tropidine-2-carboxylate, *Me* 1-ecgonine, *Et* tropinone-2-carboxylate, tropacocaine, *d-ψ*-cocaine, *dl ψ*-cocaine, *ψ*-pelleterine, *di-Et N*-methylpyrrolidine-2,5-diacetate, 2,4,6-trimethylpiperidine, *N-methyl-2,4,6-*



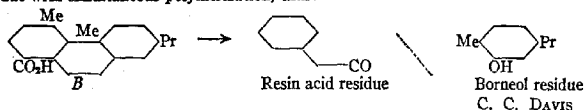
*trimethylpiperidine* (prepd. by boiling copellidine and MeI, dilg. with H<sub>2</sub>O, filtering, making alk. with NaOH, extg. with Et<sub>2</sub>O, drying over KOH and distg., b. 153–5°,  $d_4^{20}$  0.823), *N*-methyltetrahydroquinoline, bornyl acetate, isobornyl acetate, bornyl isovalerate, *N*-methylcamphidine, (prepd. by rubbing camphidine with MeI, dilg. with a little H<sub>2</sub>O, adding NaOH, extg. with Et<sub>2</sub>O, drying over KOH and distg., oil with an odor of camphor, b. 195–7°, slightly sol. in H<sub>2</sub>O with strong alk. reaction, gives a ppt. with HgCl<sub>2</sub> and H<sub>3</sub>PtCl<sub>6</sub> (picrate, short fine needles from hot H<sub>2</sub>O, m. 234°)). The data include at various temps.  $d_4^t$ ,  $n_D^t$ ,  $n_D^t$ ,  $n_D^t$ ,  $M_a$ ,  $M_D$ ,  $M_\beta - M_a$ ,  $M_\gamma - M_a$ ,  $EM_a$ ,  $EM_D$ ,  $EM_\beta - EM_a$ ,  $EM_\gamma - EM_a$ ,  $E\Sigma_a$ ,  $E\Sigma_D$ ,  $E\Sigma_\beta - \Sigma_a$ ,  $E\Sigma_\gamma - \Sigma_a$  and  $E_\beta^{20}$ . The first 8 compds. show depressions of the sp. refraction and dispersion which with slight deviations have av. values of  $E\Sigma_{refr.} = -0.5$  and  $E\Sigma_{disp.} = -9\%$ . The next 5 compds. do not have such depressions, but only because the latter are masked by other influences, such as a conjugate system. The spectrochem. values of  $\psi$ -pelletierine are similar to tropene, though structurally different. The next 5 compds. are normal, the next 3 anomalous, and the last 5 normal. Compds. contg. a 7- or 8-membered ring with a =NMe group as a bridge are characterized by a spectrochem. anomaly. C. C. D.

**Influence of papaverine on the optical activity of narcotine in acid solution.** H. E. ANNERT. *J. Chem. Soc.* 123, 376–9(1923).—The value of  $[\alpha]$  for D, Hg yellow and Hg green for narcotine (A) was detd. as follows: C<sub>7</sub>H<sub>8</sub> (c, 2) –148.75°, –154.5°, –182° at 32°; 90% EtOH (c, 0.4) —, —, –203.75° at 31°; CHCl<sub>3</sub> (c, 2) –198°, –206.5°, –242.25° at 33°; 1% H<sub>2</sub>SO<sub>4</sub> (c, 2) 57.25°, —, 65.2° at 32°; 1% HCl (c, 1) 50°, 52.2°, 56.5° at 29°. Although papaverine (B) is itself inactive, when added to a soln. of A in 1% H<sub>2</sub>SO<sub>4</sub> it causes a rapid diminution of the optical activity of the soln. The effect increases with each successive addn. of B until the ratio of B to A is 3:2, after which an increase in the ratio to 4:2 has only a slight, if any influence. It would appear that in acid soln. A and B form associated mols., which become dissociated on greater diln. The effect of B on the optical activity of A is relatively much greater in HCl than in H<sub>2</sub>SO<sub>4</sub> soln. No effect is observed when the free bases are present together in an inactive solvent such as C<sub>7</sub>H<sub>8</sub>. An acid-EtOH soln. of A is more much *d*-rotatory than the soln. of A in acid alone. C. J. WGST

**Amber.** A. TSCHIRCH. *Helvetica Chim. Acta* 6, 214–25(1923).—A survey is made of past research on the constitution of amber (A) (cf. C. A. 10, 760) in an attempt to det. the behavior of other coniferous resins during long periods of time, and to gain an insight into the constitution of resinous acids. Abietic acid (B), the chief acid of the conifers, has diminished to a very small fraction in A and that remaining has undergone autoxidation to succoxyabietic acid. From the greater part of the acids of the type of B originally present in the resin there have been formed during centuries the succinoresin (C), the *d*-borneol ester of succinosilvinic acid and a transformation product of succinic acid (D) and succinoresinol (E). No recent coniferous resin contains so great an amt. of C as A, the amt. usually lying below 10%, whereas A contains approx. 65%. This is too high in A to have been formed by resinification of oil of turpentine, and all ethereal oils are volatilized too soon. The resin acid of conifers must contain a D residue, for by dry distn. or KOH fusion, D is obtained, and since it is certain that it must be derived from a hydrated retene, it must also contain a phenanthrene nucleus. But how the side chains are orientated has not been detd. In A a transformation must have occurred, the bond between D and the residue have become loosened and an ester has been formed with simultaneous oxidation of the ring, thus:



The borneol ester may be formed in an analogous way, by coupling with a resin acid residue with simultaneous polymerization, thus:



**Castelamarin**—a bitter principle from *Castela nicholsoni*. L. P. BOSMAN. *J. Chem. Soc.* 123, 207–10(1923); cf. *C. A.* 16, 2849.—Castelamarin may be purified by crystn. from 60% EtOH or by pptn. from very dil. NaOH by dil. HCl. It contains 18.2% MeO but this group could not be split off by 15% HCl under pressure or by EtOH–NaOH. Hydrolysis with 2.5% HCl for 4 hrs. gave a minute amt. of a substance m. 166–8°. Oxidation gave a substance m. 238–40° (neither product was analyzed). The principle is of low toxicity and has only slight pharmacol. activity. C. J. W.

The structure and formation of humic acids and of coal. J. MARCUSSON. *Z. angew. Chem.* 36, 42–3(1923); cf. *C. A.* 16, 411.—Arguments are advanced in favor of M.'s theory that humic acid contains a furan nucleus. Numerous references are given.

T. S. CARSWELL

**Borneol** obtained from the magnesium compound of pinene hydrochloride. G. VAVON AND A. L. BERTON. *Bull. soc. chim.* 33, 218–28(1923).—See *C. A.* 16, 4199. E. H.

Relationship between resinification and the constitution of chemical compounds. III. New process for preparing synthetic resins (HERZOG, KREIDL) 26. Experimental plant for producing benzene from phenols (FISCHER, *et al.*) 21. Hydrolysis of glycylglycine by hydrochloric acid (LAICHNIKOV) 2. Studies on specific heats. III. Specific heat of isomeric compounds and aromatic hydrocarbons (PADOA) 2. Luminescence of compounds formed by the action of Mg on *p*-dibromobenzene and related compounds (EVANS, DUFFORD) 3. Formation of indole, and indole reactions. Behavior of indole-negative bacteria (FRIEDER) 11C.

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**Catalytic oxidation of hydrocarbons**. BARRETT Co. Brit. 189,091, Sept. 12, 1922. Aromatic hydrocarbons contg. a Me group are oxidized by passing their vapor admixed with an O-contg. gas over a catalyst comprising a compd. of a metal or metals of the fifth or sixth periodic group mixed with a compd. of another metal or metals. The mixed catalysts may be mounted on a carrier, such as pumice or asbestos, by soaking it in a soln. contg. salts—especially the org. salts—of the metals, or with an aq. suspension of the finely divided metal oxides or hydroxides, and afterwards igniting. The process applies particularly to the oxidation of toluene to BzH, a mixt. of U and Mo

oxides being used, with or without CuO, as the catalytic material. The xylene, pseudocumene, mesitylene and their halogenated derivs. are also mentioned as starting materials. The O-contg. gas may be air, O, or ozone, or mixts. of these, and steam or diluent gases may be introduced. Cf. *C. A.* **16**, 567.

**Catalytic oxidation of hydrocarbons.** BARRETT CO. Brit. 189,107, Oct. 23, 1922. Aromatic aldehydes are produced by passing the vapor of an aromatic hydrocarbon contg. substituent groups, one at least of which is an aliphatic group, in admixt. with an O-contg. gas over a catalyst comprising an oxide of a metal of the fifth or sixth periodic group, other than V. The catalysts may be prepd. by depositing a suitable salt of the metal on a carrier, such as pumice or asbestos, and igniting the deposited salt to the oxide. An O-contg. gas, air, pure O, ozone, or mixts. of these may be employed, with or without diluent gases or steam. According to example, *o*-xylene yields *o*-tolualdehyde over Mo oxide; a mixt. of *m*- and *p*-xylenes give *m*- and *p*-tolualdehydes over U oxide; pseudocumene yields 1,2-dimethyl-4-benzaldehyde over W oxide; mesitylene gives 1,3-dimethyl-5-benzaldehyde over U oxide; *p*-cymene yields *p*-tolualdehyde over U oxide; and *o*-chlorotoluene gives *o*-chlorobenzaldehyde over Ta oxide.

**Phenylglycine.** BRITISH DYESTUFFS CORPORATION, LTD. AND M. WYLER. Brit. 188,933, Nov. 3, 1921. Phenylglycine is obtained from  $C_6H_5Cl$  and  $PhNH_2$  by a modification of 173,540 (*C. A.* **16**, 1435). One mol. proportion of  $C_6H_5Cl$  is slowly pumped into a mixt. of slightly more than 1 mol. proportion of  $PhNH_2$  and a base such as milk of lime at 170–180°. The phenylglycine salt obtained is worked up in the usual manner.

**Reducing nitro to amino compounds.** D. A. LEGG. U. S. 1,447,557, Mar. 6. Vapor of a nitro compd., e. g.,  $PhNO_2$ , is passed together with H or other reducing agent in contact with a catalyst formed by fusing CuO, cooling the fused mass and breaking it into pieces, to effect reduction of the nitro compd. to the corresponding amino compd., e. g.,  $PhNH_2$ .

**Basic aluminium salicylate.** J. ALRWEG. U. S. 1,447,501, Mar. 6.  $C_6H_4(OH)CO_2Al(OH)_2$  is prepd. by reaction of equimol. proportions of  $Al(OH)_3$  and salicylic acid in  $H_2O$ , preferably with warming.

**Urea.** DENSHIRO KOBAYASHI. Japan. 40,298, Oct. 13, 1921. A homogeneous mixt. of  $CaCN_2$  (100 parts), 2–3%  $MnCl_2$  soln. (200–250 parts) and rice or wheat bran (200–300 parts) is stored in a suitable vessel for about 1 week in the summer or 2 weeks in the winter. During the storage, the fermentation of the bran begins,  $CO_2$  is evolved and  $CNNH_2$  in the material is changed into urea. The following reactions take place:  $2CaCN_2 + 2H_2O = Ca(CN.NH)_2 + Ca(OH)_2$ ,  $Ca(OH)_2 + MnCl_2 = Mn(OH)_2 + CaCl_2$ . In the hydrolysis  $MnCl_2$  acts as an accelerator and  $Mn(OH)_2$  is a catalyzer of the change of  $CNNH_2$  into urea.  $CO_2$  evolved by the fermentation of the bran reacts thus:  $CO_2 + H_2O + Ca(CNNH)_2 = 2CNNH_2 + CaCO_3$ . In the product only traces of  $CNNH_2$  and dicyanodiamide are found.

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

Walter Stanley Haines. WM. D. McNALLY. *Ind. Eng. Chem.* **15**, 425(1923).—An obituary, with portrait. E. J. C.

Periodicity of enzymes. F. SLUITER. *Arch. neerland. physiol.* **8**, 34–42(1923); cf. *C. A.* **16**, 2336.—The alternating increase and decrease of the activity of lipase from the stomach of mice and calves are studied. R. BRUTNER

**The unit of measure for enzymes.** RICHARD WILLSTÄTTER AND RICHARD KUHN. *Ber.* 55B, 509-12(1923).—For quant. evaluating the enzyme activity of invertase-contg. materials, the term sucrose unit is defined as the amt. of enzyme in 50 mg. of substance that has a time value of unity. The time value is that time required to bring 4 g. of sucrose in 25 cc. to zero optical activity. The purity of the enzyme prepn. is calcd. from the reciprocal of the sucrose unit giving the number of sucrose units in 50 mg. This method of expression is compared with the nomenclature, in which "inverting capacity" =  $(k \times \text{g. sucrose}) \div \text{g. prepn.}$ ,  $k$  being the inversion const. F. A. C.

**The mechanism of fat synthesis in the living cell.** HUGO HAEHN AND WALTER KINTROP. *Ber.* 56, 439-45(1923).—Pure cultures of the yeast fungus *Endomyces vernalis* were grown on media that yielded fat-free cells. Fat formation in the cell was followed microscopically by staining with Nile blue after incorporation of glucose and  $\text{CH}_3\text{COCOOH}$  buffered with phosphate, and glucose and  $\text{CH}_3\text{CHO}$ . Fat detns. at diff. stages were made to check the microscopic appearance. The steps in the fat synthesis from glucose are probably glucose  $\rightarrow$  pyruvic acid  $\rightarrow$  acetaldehyde  $\rightarrow$  aldol  $\rightarrow$  glycerol esters. F. A. CAJORI

**The preparation of a highly active invertase and a note on its sulfur content.** H. V. EULER AND K. JOSEPHSON. *Ber.* 56, 453-5(1923).—The juice expressed from yeast that had been autolyzed for 1 month at 35° was treated with EtOH. The ppt. was dissolved in  $\text{H}_2\text{O}$  and the resulting soln. pptd. with 8.5 g.  $\text{Al}_2\text{O}_3$ . The ppt. was washed with water and 1%  $\text{K}_2\text{AsO}_4$ . The washings carried 70% of the invertase present in the yeast.  $\text{MgCl}_2$  was added to remove the arsenic acid. This was followed by a 16-hr. dialysis, a process that diminished the enzyme activity less than 3%. The product contained 2.86% ash and 0.38% sulfur. F. A. CAJORI

**Protoplasmic hysteresis and the problem of rejuvenation.** V. RUZICKA. *Deut. med. Wochschr.* 48, 931-2(1922).—The theory of protoplasmic hysteresis, defined as the gradual increase in condensation products in the living organism from beginning of life to old age, and measured by the  $p_H$  of organs and the protein-pptg. ability of alc. on organ exts. is further tested on white rats. Rats were subjected to Steinach's operation to arrest development. After 20 or 30 months they were killed and the  $p_H$  and alc.-pptg. number of the organs detd. Litter mates served as controls. The animals operated on, "younger" because of the operation, showed lower  $p_H$  and alc.-pptg. values than the controls, results that justify the view that by a measure of the protoplasmic hysteresis the problem of rejuvenation can be attacked. F. A. CAJORI

**Enzymes and light. I. Diastase.** I. L. PINCUSSEN. *Biochem. Z.* 134, 459-69 (1923).—Various concns. of diastase with various concns. of salts and carbohydrates were exposed to the rays of a quartz lamp under various conditions of illumination. Complicated phenomena were made apparent. The action of light on the diastase is dependent on the diln., the various substances also present, and the reaction. The greatest damage done by light occurs at that reaction which is optimal for enzyme activity. **II. Urease.** I. L. PINCUSSEN AND N. KATO. *Ibid.* 470-5.—Petr.-ether extd. soy-bean meal was used as the source of the urease. The effect of different periods of illumination on urease activity in variously buffered solns. was studied. In general urease reacted to light from the Hg-quartz lamp as did diastase. F. S. HAMMETT

**Note on the isoelectric point of muscle protein.** K. O. GRANSTRÖM. *Biochem. Z.* 134, 589(1923).—The mean value obtained for myosin was  $p_H$  3.92. F. S. H.

**The influence of proteins on the coagulation of the blood.** RUDOLF SALOMON AND ERNST VEV. *Arch. Gynäkol.* 116, 317-32(1922).—*In vitro* coagulation of the blood was delayed by the proteins caseosan and aolan and by the non-proteins yatrien, placenta-optone and pituglandol. However, on dilg. to one-tenth the opposite effect, was obtained of hastening coagulation. By intravenous or intramuscular injections marked

changes were noted in the rate of coagulation. It is probable that such injections might be of practical use as a preliminary to operations by causing the blood to clot more readily.

HARRIET F. HOLMES

**Explanation of the colloidal behavior of proteins.** JACQUES LOEB. *Science* **56**, 731-41(1922).—The chemistry of proteins does not differ from the chemistry of crystalloids for the proteins combine stoichiometrically with acids and alkalis forming protein salts which dissociate electrolytically. These very large protein ions and mols. cannot diffuse freely through gels or membranes permeable to small crystalloidal ions so that an unequal distribution of the crystalloidal ions results between a protein soln. and an outside aq. soln. or between a protein gel and an aq. soln. In this unequal distribution the total concn. of crystalloidal ions is always greater inside the protein soln. or inside a gel than in the surrounding aq. soln. and this is the cause of the colloid behavior of protein solns. and protein gels. Measurements of membrane potentials have shown that this excess concn. of crystalloidal ions inside over the concn. of crystalloidal ions outside the protein soln. or gel and consequently all the effects of electrolytes on osmotic pressure, swelling, and viscosity of proteins can be calcd. with a satisfactory degree of accuracy from Donnan's membrane equil. equation. Colloid behavior can thus be explained on a mathematical basis. The anomalous "colloid" behavior was hitherto obtained because of neglect of measurement of the  $p_H$  of the solns, the detg. variable, and measurement of membrane potentials of protein solns. and gels. I. N. K.

**Nuclear and cytoplasmic oxidative enzymes and their physiological importance.** MARCEL PRENANT. *Compt. rend. soc. biol.* **87**, 972-4(1922).—In fresh tissue, both of animal and plant origin, the nucleus is incapable of oxidizing benzidine in presence of  $H_2O_2$ . Only a few hrs. before death can a bluing of the reagent be observed. S. M.

**The influence of sodium chloride on the solubility of sodium glycocholate.** EDMOND DOUMER. *Compt. rend. soc. biol.* **87**, 1097-8(1922).—Increasing the concn. of NaCl from 22 g. per l. up to 230 g. the soly. of the Na glycocholate diminished from 0.9 g. to 0.05 g. per l. S. MORGULIS

**The existence of two amylolytic enzymes in malt diastase.** ERIK OHLSSON. *Compt. rend. soc. biol.* **87**, 1183-4(1922).—The iodine reaction and the reduction reaction which change with the progress of the hydrolysis of starch with malt ext. are ascribed to two independent enzymes in the malt: one carries the hydrolysis only to the dextrin stage—a dextrinogenase; the other hydrolyzes the starch or dextrin to maltose—a saccharogenase. The reality of their sep. existence is shown by prep. malt exts. at different  $p_H$  by means of HCl or  $Na_2CO_3$ . The 2 enzymes are differently affected and in this way they can be sepd. At a  $p_H$  of about 4 the dextrinogenase is destroyed more effectively than the saccharogenase, and it is possible to get a prepn. practically free from the former. At a  $p_H$  of about 10 the saccharogenase is destroyed more rapidly, but the change at this point is not as definite and it is not possible to get a pure dextrinogenase ext. by this method. A better way of prep. the latter was found by heating an ext. of  $p_H = 6$  for 20 min. at  $70^\circ$  at which the saccharogenase is completely destroyed while the dextrinogenase is scarcely influenced. S. MORGULIS

**The specificity of dehydrogenases.** GUNNAR AHLGREN. *Compt. rend. soc. biol.* **87**, 1409-11(1922).—When muscle carefully washed is tested for its dehydrogenating power by the methylene blue method it is found ineffective against EtOH, MeOH, acetone or the lower fatty acids but is still active in the oxidation of citric, malic, tartaric, etc., acids. After renewed washing the muscle tissue loses its effect on these acids while still active in oxidizing lactic and hydroxyglutaric acids. In further washing, only succinic and glycerophosphoric acids are oxidized. There are thus probably 4 groups of dehydrogenases. S. MORGULIS

**Acid and alkali combinations with protein.** MASAJI TAKEDA. *J. Biochem.*

(Japan) 2, 103-15(1922).—Crystallized ovalbumin dialyzed under pressure for 4 weeks was used in these expts. The influence of acids and alkalis on the number of ions in a mixt. with protein was studied by the cryoscopic method. The usual procedure was to add to 32 cc. of the albumin either acid or base and then enough  $H_2O$  to bring the vol. up to 64 cc. With a final HCl concn. of 0.004 *N* and 0.75% albumin the addition of the latter has no effect on the freezing point of the acid. With a concn. of 0.008 *N* HCl the albumin-acid mixt. has a smaller lowering of the freezing point and this diminishes gradually with the HCl concn. until its concn. reaches 0.016 *N*. The combinations of albumin with NaOH show a stronger tendency to dissociation, and in this case there is no evidence of a suppression of ionization until a concn. of 0.03 *N* has been reached. When the concn. of acid or alkali was very small it could be invariably shown that the combination with the albumin had a greater lowering of the freezing point than the acid or alkali alone. This fact is interpreted in this way that during dialysis a number of protein mols. combine with each other by their free COOH and  $NH_2OH$  groups, and under the influence of traces of acid or base these unions break up liberating a certain number of protein mols. which then contribute to the lowering of the freezing point. Since the expts. indicate that a max. of ionization occurs at an albumin concn. of 0.75% and 0.004 *N* HCl it follows that at this concn. there must be an equal number of Cl ions and albumin ions, and since under those conditions the depression of the f. p. was 0.007 the mol. wt. of the albumin is calcd. as 1982. The mol. wt. calcd. from the S content of albumin is 2133. S. MORGULIS

Action of thorium X on diastases and on bacteria. J. P. AVERSENQ, L. JALOUSTRÉ AND E. MAURIN. *Compt. rend.* 176, 193-5(1923).—Expts. with controls proved that Th X, 100%, promoted the action of salivary ptyalin and of pancreatic amylase *in vitro* in 24 hrs. at 37°. Th X, 50%, increased the amt. of  $NH_3$  in 50 cc. of urine, increased the oxidation by the oxidases of the blood serum, and the oxidases of the saliva. The change of starch to sugar by amylase of barley is increased by Th X, 10%, but Th X 400%, appears to have no action. Th X has a similar activating effect upon emulsin and accelerates the development of staphylococci and gonococci and prolongs the vitality of spermatozooids. L. W. RIGGS

Origin of the humin formed by the acid hydrolysis of proteins. VII. Hydrolysis in the presence of ketones. R. A. GORTNER AND E. R. NORRIS. *J. Am. Chem. Soc.* 45, 550-3(1923); cf. *C. A.* 15, 673.—Fibrin was hydrolyzed alone and in the presence of  $Me_2CO$  and  $MeCOPh$  and the N distribution in the products detd. The N distribution as measured by the Van Slyke method is not altered by hydrolysis in the presence of ketones. The acid-insol. humin of a protein hydrolysis is apparently not formed, therefore, by the interaction of a ketone with tryptophan but is probably due to its interaction with some as yet unidentified aldehydic component of the protein mol. C. A. R.

Some novel aspects of colloidal protection (ALEXANDER) 2. Dielectric constants of some materials of biological interest (FÜRTH) 2.

HÖBGER, RUDOLF. *Physikalische Chemie der Zelle und der Gewebe*. 5th Ed. revised. Part I. Leipzig: Wlb. Engelmann. 544 pp. M 575.

LUMIÈRE, AUGUSTE. *Theorie colloïdale de la biologie et de la pathologie*. Paris: Etienne Chiron. 220 pp. Fr. 12.

\* MICHAELIS, LEONOR. *Einführung in die Mathematik für Biologen u. Chemiker*. 2nd Ed. revised. Berlin: Julius Springer. 318 pp. M 147.

## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

Titration of urea in urine for clinical purposes. E. FRIEDLÄNDER. *Münch. med. Wochschr.* 68, 1225-6(1921).—Directions are given for titration with  $HgCl_2$ . • S. A.

A polychemical urobilin reaction which can be done anywhere. TH. HARTMANN. *Münch. med. Wochschr.* **68**, 1558-9(1921). S. AMBERG.

Vital staining with Janus-green. M. W. WOERDEMAN. *Nederland. Tijdschr. Geneeskunde* **66**, I, 2450-3(1922).—The physiol. objects used for staining are various animals from the group of *Vorticellidae*. "Janus-green" is dimethylsafranineazodimethylaniline. By reducing agents the azo group is decomposed and diethylsafranine is formed. The granulae in the cell are stained bluish green; the feeding-vacuoles exhibit an intense color. The cellular body exhibits only a feeble greenish color which is likely to be due to the reduction of a part of the dye. The nucleus is not stained unless the cell is dead. R. BRUTNER

An accurate method of determining small amounts of ethyl ether in air, blood, and other fluids, together with a determination of the coefficient of distribution of ether between air and blood at various temperatures. H. W. HAGGARD. *J. Biol. Chem.* **55**, 131-43(1923).—The method depends upon the oxidation of  $\text{Et}_2\text{O}$  by  $\text{I}_2\text{O}_5$  at  $200^\circ$ , with liberation of I which is caught in a soln of KI. 30 min. arc required for a detn. The sample should not contain more than 5-6 mg.  $\text{Et}_2\text{O}$ . With 1-1.5 mg. the error was  $\pm 3\%$ . At ordinary temps. and pressures,  $\text{Et}_2\text{O}$  vapor behaves as a true gas. The ratio of  $\text{Et}_2\text{O}$  in air to  $\text{Et}_2\text{O}$  in  $\text{H}_2\text{O}$  was at  $21^\circ$ , 1:30.95; at  $26^\circ$ , 1:25.06; at  $32^\circ$ , 1:18.92; at  $37^\circ$ , 1:15.61; at  $38.5^\circ$ , 1:15.15 and at  $40^\circ$ , 1:14.54. With defibrinated dog blood, the ratios were at  $26^\circ$ , 1:23.40; at  $32^\circ$ , 1:18.85; at  $37^\circ$ , 1:15.20; at  $38^\circ$ , 1:14.95. Calcs. from the value for the anesthetic tension of  $\text{Et}_2\text{O}$  in air (cf. Boothby, *C. A.* **8**, 1617) (assumed to be at  $20^\circ$  and satd. with  $\text{H}_2\text{O}$ ) indicate that the concn. of  $\text{Et}_2\text{O}$  in the blood during full anesthesia is 2833 mg. per l. of blood. I. GREENWALD

A simple method for the determination of lactic acid in gastric contents. R. ÈGE. *Biochem. Z.* **134**, 476-88(1923).—The test meal is thoroughly mixed by shaking. 10 to 15 cc. are measured out, made acid with 1 drop of concd. HCl for each 10 cc. mixt. to set free combined lactic acid and filtered. 5 cc. of the filtrate is transferred to a separatory funnel, 4 drops of Me-violet and 50 cc. of acid-free  $\text{Et}_2\text{O}$  are added and the mixt. is well shaken. The  $\text{H}_2\text{O}$  is allowed to run off. The  $\text{Et}_2\text{O}$  contains 50% of the original lactic acid since the partition of the acid between  $\text{H}_2\text{O}$  and  $\text{Et}_2\text{O}$  is 10:1. This  $\text{Et}_2\text{O}$ -dissolved lactic acid is washed out with  $\text{H}_2\text{O}$  and detd. by titration. F. S. H.

The role of washing in the determination of the osmotic resistance of the erythrocytes. U. STRASSER. *Biochem. Z.* **134**, 541-5(1923).—The differences in the resistance values of washed and unwashed erythrocytes are generally too small to be of significance in clinical studies. In icterus and pernicious anemia, however, both methods are advocated. None of the so-called physiol. salt solns. leave the corpuscles undamaged. F. S. HAMMETT

Colorimetric and pharmacologic evaluation of the adrenaline content of the adrenals. B. FROWEIN. *Biochem. Z.* **134**, 559-66(1923).—The colorimetric method gives too high results and should be replaced by the blood pressure detn. F. S. HAMMETT

Methodology of blood alkali determination. H. GALLWITZER. *Biochem. Z.* **134**, 590-600(1923).—A comparison of the titration methods of Van Slyke (*C. A.* **13**, 2052) and Rohonyi (*Münch. med. Wochschr.* **67**, 51(1920)) with the gas analysis method of Bancroft showed that the former methods give too high and too low values, resp. The deviations from the values obtained by gas analysis were inconst. This method then is the more simple and exact. F. S. HAMMETT

The gradual darkening of hematin solutions in colorimetric estimations, and its prevention. H. C. GRAM. *Acta Med. Scand.* **56**, 52-70.—The darkening of hemoglobin solns. is not attributed to change of oxyhemoglobin to hematin. It is affected by strength of acid and to a less degree by temp. It may be prevented in the Autenrieth method by addn. of 2 cc. of 3%  $\text{H}_2\text{O}_2$  to 98 cc. of the HCl used. The wedge used for

comparison must be specially graduated. The modification is not applicable to the Sahli method. J. C. S.

**Micro-analyses by Bang's methods.** I. LUDWIG PETSCHACHER. *Biochem. Z.* **131**, 116-23(1922).—The estn. of chlorides by micro-analysis in drops of blood gives sufficiently accurate results, but the estn. of dextrose and residual N is not sufficiently accurate. J. C. S.

**Detection of urea in tissue by means of xanthidrol.** M. BONNET AND J. HAUSHALTER. *Compt. rend. soc. biol.* **86**, 395-7(1922).—For the microchem. detection of urea, the fixation of the tissue in a 10% soln. of xanthidrol in EtOH and pure AcOH in the ratio 1:7 is recommended. J. C. S.

**Identification of alanine by crystallo-chemical analysis.** IV. S. IAICHNIKOV. *J. Russ. Phys. Chem. Soc.* **52**, 145-7(1920).—Polarimetric identification of active alanine is sometimes impossible owing to the marked opalescence of the soln. In such case, use may be made of crystallographic measurements. The results of l's measurements are compared with those of Groth and of Fischer (*Ber.* **39**, 453-74(1905)). J. C. S.

**Qualitative and quantitative demonstration of blood in urine.** A. JOHANNESSEN. *Ugesk. Laeger* **83**, 1613(1921).—The reagent recommended is prepd. by adding 1 g. of phenolphthalein and 25 g. of KOH to 100 cc. of distd. water and then boiling with 10 g. of zinc dust until decolorized. After filtration, an equal vol. of 96% alc. is added. This soln. keeps for six months. Immediately before use 1 cc. of  $H_2O_2$  is added to each 9 cc. Equal vols. of the reagent and the suspected urine are mixed; if blood is present up to 1 in 20,000 or 1 in 30,000 a pinkish red color is formed. With even in water, positive reaction is obtained with dilns. as high as 1 in 500,000. Cu even in traces interferes with the test. J. C. S.

**Determination of organic acids of soluble calcium salts.** R. GOFFON AND F. NEPVEUX. *Compt. rend. soc. biol.* **87**, 1173-4(1922).—A 10% suspension of feces is prepd. in a mortar. To 50 cc. of this homogeneous and dil. mixt. are added 10 drops of a concd. soln. of  $Al_2(SO_4)_3$  and a few drops of phenolphthalein, then a concd. soln. of Ca succrate (20 g. sucrose, 5 g.  $Ca(OH)_2$  and 100 cc.  $H_2O$ ), until a distinct alk. reaction is obtained. This is filtered and the filtrate, to which are added 5 drops of a 0.5% phenolphthalein, neutralized to a faint pink color. This is then titrated with 0.1 N HCl with 5 cc. of a 0.02% orange IV until a shade of orange is obtained in a vol. of 60 cc. which corresponds to that given by 1.2 cc. of the 0.1 N acid with the same amt. of indicator and also in 60 cc. From the number of cc. used for titration 1.2 cc. is subtracted and the difference multiplied by 4 gives the quantity of org. acid in 10 g. of the salt. Only such acids as lactic, succinic, butyric, acetic form the sol. Ca salts while  $H_2CO_3$ ,  $H_3PO_4$ , and higher org. acids yield insol. salts, which are filtered off. The accuracy of the method was tested by adding known amts. of org. acids and recovering them quantitatively. S. MORGULIS

**A practical method for the macroscopic observation of the beginning of coagulation of blood.** MAURICE PERRIN AND ALFRED HANNS. *Compt. rend. soc. biol.* **87**, 1215-6(1922).—Fifteen drops of blood, collected directly from a vein with a needle of fine bore, are placed on slides, 1-2 drops on each. The slides are immediately placed under a bell-jar, and about 10 min. later the slides are removed one by one and the blood is tested with a fine rod. At the beginning of the coagulation filaments appear which cannot be spread or dissociated from the rest by the rod. The method is believed to be very accurate. The usual coagulation time for normal human blood by this method is within the limits of 15 and 20 min. After an intravenous injection of 1 cc. of an ext. of the posterior lobe of the hypophysis the coagulation began only 17 min. after the blood was drawn and was not completed until after 31 min. S. MORGULIS

**A modification of Fuld's method for measuring the amount of pepsin.** RICH. EGG.



*Compt. rend. soc. biol.* **87**, 1217-9(1922).—Ten cc. of an edestin soln. is made up with tartaric acid so as to give the optimum reaction for the peptic reaction. The soln. seems to have good keeping qualities and can be used for a long time. This is added to test-tubes of uniform diam. (21 mm. outside) and is mixed with 1 cc. of the peptic soln. The tube is then incubated at 40° for 30 min. when, in order to stop the digestion, it is quickly submerged in a boiling water bath for 5 min. The degree of digestion is now detd. by titrating with 20% NaCl or satd.  $(\text{NH}_4)_2\text{SO}_4$  (70 g. to 100 cc.  $\text{H}_2\text{O}$ ). The end point is the appearance of the ppt. in the tube. The amt. of salt soln. added to obtain this point is read off from the buret. The edestin soln. is prepd. as follows: 2 g. of edestin are added to 300-400 cc.  $\text{H}_2\text{O}$ ; 75 g. tartaric acid and 10.5 g. of Rochelle salt are dissolved in about 500 cc.  $\text{H}_2\text{O}$  which is heated to boiling and poured while boiling into the first suspension. The edestin dissolves at once. Ten cc. of  $\text{HgCl}_2$  1% is added and the whole made up to 1 l. and filtered. With Arnour's pepsin prepn. contg. from 0 to 1.8 mg. of the substance per 1 cc. a table is worked out giving the titration values. The peptic activity of an unknown soln. is detd. by comparing with the results recorded in the table.

S. MORGULIS

Comparison of the urea determination in blood and in urine by the sodium hypobromite and by the xanthidrol methods. F. SCHMID. *Compt. rend. soc. biol.* **87**, 1369-71(1922).—The results by both methods are thought to be in good agreement, except when serum is used which had been kept several hrs. before analysis. In this case much higher values are found by the hypobromite method.  $\text{NH}_3$  affects the results by this method, but in blood with a low and practically const. content the urea detn. is corrected by subtracting 1 mg. per 100 cc. It is more difficult to get accurate results for urine, where the  $\text{NH}_3$  content is not const.

S. MORGULIS

A micro-ureometer. L. AMBARD AND F. SCHMID. *Compt. rend. soc. biol.* **87**, 1374-7(1922).—The app. consists of a small glass cup attached to a tube by means of a ground glass stopper. The cup is closed by a rubber cap. With the aid of glass beads the capacity of the cup can be varied, but it is usually adjusted to 6 cc. Four cc. of liquid is introduced into the app. and by pressing on the rubber cap air bubbles are driven out. One cc. of a soln. of NaBrO is then added. The gas evolved causes the relaxed rubber cap to expand. The evolved gas is now collected under water into a funnel-shaped tube, the tubular part of which is calibrated into  $1/20$  cc. The technic that is necessary to cause all the gas set free in the reaction to accumulate into this tube is fully described. Good detns. can be made with 0.1 cc. of gas. With ordinary blood 4 cc. of plasma pptd. with an equal vol. of  $\text{CCl}_3\text{COOH}$  is sufficient to measure the urea content. Three procedures are open with this app. (1) The O set free is absorbed with  $\text{NaHSO}_3$  and the remaining vol. should correspond to the theoretical vol. of N. (2) In view of the regularity of the O liberation, a correction of 0.007 cc. for gas evolution up to 0.1 cc. and of 0.015 cc. for quantities between 0.15 and 0.35 cc. makes the extra O absorption unnecessary. (3) The gas produced by different quantities of urea is measured and the amt. of urea in the unknown sample is calcd. by interpolation.

S. MORGULIS

On the disintegration of urea and of other nitrogenous substances in the urine by means of vapor distillation. MALTE LJUNGDAHL. *Compt. rend. soc. biol.* **87**, 1411-3 (1922).—Expts. made with known quantities of  $\text{NH}_3$  in the form of its salts to which urea, uric acid or glycine has been added show that the  $\text{NH}_3$  is quantitatively recovered by a 5 min. vapor distn. and that these various substances do not appreciably influence the results. The method is considered of importance because, unlike the formol titration, it gives the true  $\text{NH}_3$  content, and it also has the advantage over the aeration method in that it requires very much less time. The total N can be detd. after digesting 1 cc. of urine in the usual manner and distg. the  $\text{NH}_3$  set free with alkali by steam.

S. MORGULIS

**A method for the determination of ammonia in the urine.** MALTE LJUNGAHL. *Compt. rend. soc. biol.* **87**, 1414-6 (1922).—The method utilizes the principle of distn. by steam. One cc. of urine in a small Kjeldahl flask (50 cc.) is made alk. with 2 cc. of a 10-15% soln. of  $\text{Na}_2\text{CO}_3$ . The Kjeldahl flask is connected to a 1 l. Florence flask in which  $\text{H}_2\text{O}$  is boiled and the steam thus generated conveyed through tubular connections to the bottom of the Kjeldahl flask. The distn. is carried out for just 5 min., which is sufficient to drive off every trace of the  $\text{NH}_3$  present. The distillate is received into 2 cc. of 0.1 *N* acid and this is titrated against 0.1 *N* alkali with methyl orange as indicator.

S. MORGULIS

**Separation of globulins from horse serum.** A. VILLA. *Compt. rend.* **175**, 728-31 (1922); cf. *C. A.* **14**, 3092; **16**, 721.—The proteins of the serum are prepd. as follows: The serum is dild. with an equal vol. of water, cooled to  $0^\circ$ , poured into 3 vols. of acetone at  $-10^\circ$  and the mixt. centrifuged in a Jouan app. The clear liquid contg. the salts and fats is decanted from the ppt. which contains the total proteins and the latter extd. with  $\text{Et}_2\text{O}$ , then with acetone. The proteins are then dissolved in water up to the original vol. of the serum. The optimum amt. of 0.01 *N* HCl to give a max. pptn. is detd. on 2 cc. samples of the protein soln. by adding from 1.5 to 3.0 cc. of the HCl and water if necessary to make the vol. 5 cc. The main soln. is then treated with a proportional amt. of the HCl, which ppt. the globulin. The pptd. globulin is washed by centrifugation and purified by soln. in a measured amt. of 0.1 *N* NaOH and repptd. by a measured amt. of 0.1 *N* HCl. This treatment is repeated until the supernatant liquid shows only a trace of protein upon the addn. of an excess of acetone. The protein in dil. HCl is again pptd. by acetone in the cold to eliminate the HCl and salts, which are retained by the acetone, the ppt. is centrifuged, washed with ether and suspended in water. The portion insol. in water is dissolved in acid and repptd. by acetone, yielding a second fraction of the globulin. The clear liquid from the first pptn. contains serum-albumin which may be purified by fractional pptn. with acetone. Analyses of 6.64 g. of serum protein, from which the fats and salts had been removed, gave globulin insol. in 1/1250 HCl 24.3%, globulin sol. in 1/1250 HCl 27.1, serum-albumin 39.9, loss in washings 8.7.

L. W. RIGGS

**Precipitin reaction for thyroglobulin.** LUDWIG HEKTOEN AND KAMIL SCHULHOF. *J. Am. Med. Assoc.* **80**, 386-7 (1923).—The antigenic properties of thyroglobulin, carefully prepd. from beef, swine and human thyroids in the usual way, were tested upon rabbits. The results indicate that human thyroglobulin, prepd. as described, contains a main strictly sp. antigen and also lesser antigens that in the rabbit may call forth precipitins for thyroglobulins of other species. Perhaps closer study may reveal several thyroglobulins in other species also; but beef and swine thyroglobulins used in these expts. acted as strictly sp. antigens.

L. W. RIGGS

**Simple and rapid test for albumin and other urinary proteins.** WM. G. EXTON. *J. Am. Med. Assoc.* **80**, 529-30 (1923).—To make a l. of the reagent, dissolve 200 g.  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  in 700-800 cc. of water, cool to  $35^\circ$  and add 50 g. of sulfosalicylic acid, stirring until dissolved and make up to 1 l. Equal vols. of the urine and reagent are mixed and warmed. Boiling does not spoil the test but is not necessary. The presence of albumin is shown by a cloudiness, the turbidity being proportional to the concn. of the albumin. Ten advantages over other reagents for detecting albumin are stated.

L. W. RIGGS

**Simple process for the detection of urobilin in urine.** G. RODILLON. *J. pharm. chim.* **26**, 379-81 (1922).—Grimbert's technic (*C. A.* **5**, 2264) is modified. To a given vol. of urine in a test-tube add an equal vol. of reagent A (15 g.  $\text{ZnO}$ , 250 cc. 95%  $\text{EtOH}$ , 15 cc. cryst.  $\text{AcOH}$ , filter after 48 hrs.), agitate, add 1 drop of reagent B (Codex tincture of 1 dild. with 95%  $\text{EtOH}$  to 0.1), mix, then add  $\text{CHCl}_3$  (0.1 of the total vol.),

shake and note the emerald green fluorescence of the bottom layer in strongly convergent light. With albuminous urine, mix it with an equal vol. of A, shake, filter and proceed as before.

S. WALPBÖRT

Freezing-point determinations on small quantities of liquid with Dekhuyzen's cryoscope (COHEN-TERVAERT) 1.

ABDERHALDEN, EMIL. *Handbuch der biologischen Arbeitsmethoden. Chemische Methoden. Spezielle analyt. u. synthet. Methoden. Eiweissabbauprodukte u. verwandte Verbindungen. Die gasometrische Bestimmung von primärem aliphat. Aminostickstoff u. ihre Anwendung auf physiol. chem. Gebiete*, DONALD D. VAN SLYKE. *Alkalimetrische Bestimmung von Aminosäuren u. Peptiden*, RICHARD WILLSTÄTTER. *Biogene Amine (Fäulnisbasen, Extraktivstoffe, Harnbasen)*, MARKUS GUGGENHEIM. *Nachweis, Darstellung u. Bestimmung methylierter Aminosäuren u. Betaine in Tier- u. Pflanzengewebe*, GEORG TRIER. *Darstellung einiger biochemisch wichtiger Substanzen aus Melasse u. Melasseschlempe*, FELIX EHRLICH. *Biologisch wichtige Aminosäuren, die im Eiweiss nicht vorkommen. Abbaustufen von solchen u. von im Eiweiss vorkommenden Aminosäuren, Nachweis, Bestimmung u. Darstellung der von natürlichen u. sonstigen wichtigen Aminosäuren ableitbaren Abbauprodukte*, ERNST B. H. WASER. 263-778 pp. *Physikalisch-chemische Methoden. Methoden zur Untersuchung des Verhaltens gelöster Stoffe. Die apparative Einrichtung zu physikalisch-chemischen Arbeiten*, PAUL HIRSCH. *Bestimmung der Acidität und Alkalität*, ANDOR FODOR. *Messung von  $p_H$  mit Indikationen ohne Puffer. Die elektrometrische Titration*, LEONOR MICHAELIS. *Potentiometrische Bestimmung von Ionenkonzentrationen*, CARL DRUCKER. 353-556 pp. *Angewandte chem. u. physikal. Methoden. Methode zur quantitativen Bestimmung d. Stoffwechsels d. Gesamtorganismus von Organen und von Zellen. Stoffwechsel. Stickstoffwechsel des Menschen. Der Wasserwechsel des Menschen*, ADOLF LOEWY. *Stoffwechselversuche an Tieren*, WILHELM VÖLTZ. 195-330 pp. *Angewandte chemische und physikalische Methoden. Methoden d. Fermentforschung. Allgemeine Darstellungsmethoden der Fermente*, SIGMUND FRÄNKEL. *Die Capillarisation zur Unterstützung mikrochem. Arbeiten und zur Untersuchung von Fermenten*, JOHANN GRÜSS. *Refraktometrische Untersuchungen fermentativer, bakterieller, toxischer und ähnlicher Wirkungen*, EMIL REISS. *Die mikro-morphologischen Methoden der Fermentforschung im tierischen und pflanzlichen Organismus*, SIEGFRIED GRÄFF. 142 pp. *Nachweis und Bestimmung der Gifte auf Chemischem Wege*, WILHELM AUTENRIETH. Berlin and Vienna: Urban and Schwarzenberg.

## C—BACTERIOLOGY

A. K. BALLS

Recent investigations on the oxidation of sulfur by microorganisms. J. G. LIPMAN. *Ind. Eng. Chem.* 15, 404-5 (1923).—The S-oxidizing organism *Thiobacillus thiooxidans* exhibits marked tolerance for  $H_2SO_4$ ; the activities are not seriously retarded until a 5% acid concn. is reached. Expts. conducted on different soils and under varying conditions show that inoculated S is much more effective than equiv. amts. not inoculated. Biol. oxidation of S has been employed as a means of producing sol. phosphates. Addition of the organism to some Oregon soils has made the elements much more available for crops through increased oxidation. Expts. on 'black alkali' soils demonstrated that carbonates disappeared, a change in  $p_H$  from 8.8 to 7.9 resulted and the permeability of the soil to  $H_2O$  improved 30-40%. The solution of soil problems, plant diseases and insect control by means of the use of inoculated S are discussed

PAUL BOONE

Nature of the bacteriophagic principle. R. BRUYNOGHE. *Compt. rend. soc. biol.*

85, 258-60(1921); *Physiol. Abstracts* 7, 70.—The transmission of the bacteriophagic principle has been explained as due (1) to the action of an ultramicroscopic organism parasitic on the bacterium (d'Herelle); (2) to the presence within the bacterium of a pro-diastase rendered active by a sol. substance contained in the intestines (Kabeshima); (3) to the presence of an enzyme secreted by the bacterium (Bordet and Ciuca). B. favors the first view on account of the non-specificity of the principle. H. G.

**Decomposition of tryptophan by staphylococci without the production of indole.** S. BAYNE-JONES AND PAULINE ZINNINGER. *Abstracts Bact.* 5, 3(1921).—Many strains of staphylococci were grown in media contg. tryptophan as the only source of N but in no case was indole produced. J. S. H.

**Behavior of some amino acids towards oxygenated yeast.** FRITZ LIEBEN. *Biochem. Z.* 132, 180-7(1922).—Unlike lactic acid, amino acids are not quickly destroyed by oxygenation of their soln. in presence of yeast cells. J. C. S.

**Formation of indole, and indole reactions. Behavior of indole-negative bacteria.** WALTHER FRIEBER. *Centr. Bakt. Parasitenkunde* 87, 251-77(1921).—In an investigation of the formation or non-formation of indole by bacteria, the principal reactions for indole were examd. using indole, indole derivs. substituted in the 2-position (2-methylindole, indole-2-carboxylic acid), indole derivs. substituted in the 3-position (skatole, *p*-indole aldehyde, indole-3-acetic acid, indole-3-pyruvic acid, indole-3-ethylamine, indole-3-alanine, indole-3-glycylalanine), and indole derivs. substituted in the 2- and 3-positions (indole-2,3-dicarboxylic acid, 2-methylindole-3-alanine, indoxyl-carboxylic acid, isatin). The Na nitroprusside reaction is the most sp., being given only with the free indole nucleus. The Ehrlich reaction (*p*-dimethylaminobenzaldehyde), the vanillin, and the naphthaquinone reactions only require the 3-carbon atom to be free, while the Salkowski reaction only requires the 2-carbon atom to be free. All indole-negative bacteria give the positive Salkowski reaction, probably on account of the formation of indoleacetic acid. The decompn. of tryptophan by indole-positive bacteria is probably accomplished in two stages with indoleacetic acid as an intermediate product. In the presence of easily assimilable C compds., indole-positive bacteria may only perform the first stage of tryptophan decompn. It is unnecessary to assume an inhibition of proteolysis by carbohydrates. No inhibition of the formation of indoleacetic acid by indole-negative bacteria is shown by carbohydrates. Of the bacteria hitherto described as indole-forming, a large no. form indoleacetic acid only. J. C. S.

**Factors governing the fat content of bacteria and the influence of fat on pellicle formation.** L. W. LARSON AND W. P. LARSON. *J. Infectious Diseases* 31, 407-15 (1922).—The results given in this paper seem to establish the general law for all bacteria that carbohydrates and glycerol are converted into fats or fat-like substances only when they are not fermented by the organisms. The fat content of the tubercle bacillus bears no relation to the virulence of the organism but is detd. by its biologic action on the glycerol in the medium. The acid-fast staining properties of the tubercle bacillus are due not to its high fat content but probably to the character of the fats or other substances present. Pellicle formation by bacteria is probably detd. by the surface tension of the medium on the one hand and the fat content of the organisms on the other. The methods of fat extn. used may have taken out substances other than fats or may not have extd. all the fats, but results are comparable. All the exts. are called fats. JULIAN H. LEWIS

**Bacterial autolysis.** W. S. STURGES AND L. F. RETTYGER. *J. Bact.* 7, 551-77 (1922).—The nitrogenous changes occurring in autolyzing bacterial suspensions were followed in a quant. way. The quant. biuret test of Vernon and the Sørensen titration have proved of greatest value. The Van Slyke detn. of amino N was employed to

advantage, although the material to be analyzed was not particularly suited to this method. Electrical cond. increased during autolysis but not in proportion to the amt. of amino N formed by the hydrolysis of protein. Proteolytic bacteria of the type *Erythrobacillus prodigiosus*, *Pseudomonas pyocyanea*, and *B. subtilis* autolyze rapidly. *B. coli* undergoes slight changes which may be autolytic in nature, but which at best involve only a small part of the complex nitrogenous constituents of the cell. The pathogenic cocci, pneumococcus, gonococcus and meningococcus, undergo an actual autolysis with a breaking down of the protein or protein-like substances of the bacterial cells.

JOHN T. MYERS

**Salt effects in bacterial growth. III. Salt effects in relation to the lag period and velocity of growth.** J. M. SHERMAN, G. E. HOLM AND W. R. ALBUS. *J. Bact.* 7, 583-8(1922); cf. *C. A.* 17, 121.—The accelerating effect of certain salts upon the growth of *B. coli* is due primarily to an increase in the velocity of growth of the organism during the period of max. multiplication. The same salts also usually decrease the duration of the preliminary latent period.

JOHN T. MYERS

**Certain phases of nitrogenous metabolism in bacterial cultures.** G. C. DE BORD. *J. Bact.* 8, 7-45(1923).—The presence of glucose in peptone media increases the rate of production of amino N in growing cultures of *B. coli*, *Ps. pyocyanea*, *B. subtilis*, *C. botulinum*, and *C. sporogenes*. The amino N in bacterial cultures is an approx. index under certain conditions of proteolysis. The Folin method for the detn. of amino N is applicable to peptone media. The  $\text{NH}_3$  found in bacterial cultures is not a reliable index of bacterial proteolysis. The presence of fermentable carbohydrate in bacterial cultures affects the nitrogenous metabolism. Some bacteria destroy glucose without a marked increase in H-ion concn. Hence  $p_H$  is not an index of glucose destruction.

J. T. MYERS

**Bacteriophage phenomena.** ANN G. KUTTNER. *J. Bact.* 8, 49-101(1923).—It is uncertain whether the bacteriophage is a living virus or something in the nature of a chem. autolysin, but the evidence points toward the latter theory. The phenomenon can be initiated by normal tissue exts. from guinea pigs, and normal rabbit sera. The high resistance to glycerol, acetone, alc., and  $\text{CHCl}_3$  was confirmed. High potency antilytic sera were not obtained.

J. T. MYERS

**New bacillus for the fixation of nitrogen.** GEORGES TRUFFANT AND N. BEZSSONOFF. *Compt. rend.* 175, 544-6(1922).—Tubes of glucose agar inoculated with Versailles garden soil contained a bacillus with the following characteristics: small, rod-shaped, Gram-positive, resembles *Proteus vulgaris*, aerobic, motile, liquefies gelatin, culture colonies are of a special form, white on gelose and on potato, assimilates mannose, glucose, sucrose, levulose and lactose, fixes atm. N at the rate of 2 to 7 mg. per g. of carbohydrate consumed, the variations depending on the kind of sugar used and being, within limits, inversely as the concn. of the sugar. This bacillus is an active denitrifying agent, possesses a diastase, produces  $\text{EtOH}$  and  $\text{AcOH}$  in the liquid nutritive medium and is abundant in the soil. As this organism is clearly different from bacteria hitherto described, the name *Bacillus truffanti* is proposed.

L. W. RIGGS

**Importance of the organic ammonium salts in the production of pyocyanin by the pyocyanic bacillus.** A. GORIS AND A. LIOT. *Compt. rend.* 176, 191-3(1923); cf. *C. A.* 16, 429.—Cultures of the bacillus on gelose in the presence of equiv. amts. of  $\text{NH}_4$  carbonate, chloride, sulfate, nitrate and phosphate were negative. In the presence of sugars or alcohols a moderate development took place and the medium became acid to litmus. With both carbohydrates and  $\text{NH}_4$  salts of mineral acids present the development of the bacillus was abundant, especially in the tubes contg.  $\text{NH}_4\text{NO}_3$  or  $(\text{NH}_4)_2\text{CO}_3$ . Cultures in the presence of carbohydrates and  $\text{NH}_3$  in amts. equiv. to that used in the  $\text{NH}_4$  salts were too alk. By adding half as much  $\text{NH}_3$  or less, the bacillus

slowly developed and at the end of 6 days the culture showed a sharp green color, but only in the presence of glucose, levulose or mannitol. The production of acids necessary to neutralize the  $\text{NH}_3$  required a number of days, but when the org.  $\text{NH}_4$  salts were formed the production of pyocyanin was rapid. Tests with urea and with glycine indicate that the bacillus produces a urease which transforms these substances into  $(\text{NH}_4)_2\text{CO}_3$ , which in turn forms org. salts with the acids derived from the sugars. Apparently the formation of org. salts of  $\text{NH}_4$  is a necessary step in the nutrition of the pyocyanic bacillus.

L. W. RIGGS

**Microbial metabolism of lactic and pyruvic acids.** E. AUBEL. *Compt. rend.* 176, 332-5(1923).—A bacterium isolated from water of the Paris supply was grown on a medium consisting of glucose 30 g.,  $\text{NH}_4\text{Cl}$  5,  $\text{H}_2\text{KPO}_4$  1,  $\text{MgSO}_4$  1 and water up to 1000 cc. This was sterilized and milk of  $\text{CaCO}_3$  added. During the first 7 days the culture gave the tests for pyruvic acid, being strongest on the 4th day and absent after the 7th day. The presence of lactic acid was not observed until the 6th day and was in larger amt. on the 10th and 15th days. These results, and those obtained by cultures on pyruvic acid and on lactic acid raise several questions demanding further study.

L. W. RIGGS

**Does nitrification occur in sea water?** C. B. LIPMAN. *Science* 56, 501-3(1922).—Culture media inoculated with sea water show that nitrifying bacteria are either absent from sea water or they cannot function in a soln. of such concn. Since it will be shown in a forthcoming paper that bacteria can withstand high salt concns., the first supposition is probably correct. It was found that culture media inoculated with calcareous sand underlying the same sea water and therefore in equil. with it, contained vigorous nitrifying organisms.

L. W. RIGGS

**Oxidation of selenium by a new group of autotrophic microorganisms.** J. G. LIPMAN AND S. A. WAKSMAN. *Science* 57, 60(1923).—Among the strictly (obligate) autotrophic bacteria which derive their energy only from the oxidation of inorg. materials are the nitrite, and nitrate, oxidizers, and the S-oxidizing organism *Thiobacillus thiooxidans*. To these may be added a group able to derive their energy from the oxidation of Se.

L. W. RIGGS

**Lactic acid bacteria isolated from cherry macerations.** C. SCHWEIZER. *Mil. Lebensm. Hyg.* 13, 293-309(1922).—Six species of lactic acid bacteria were isolated from cherry macerations. (Cf. *C. A.* 16, 986.) All of the species produced lactic acid as well as volatile acids to which the compn. of cherry brandy was attributed. Morphological and cultural studies led to the following species: *Lactobacterium paucifermens* var. *cerasi*, *Lactobacterium cerasi* I nov. sp., *Lactobacterium cerasi* II nov. sp., *Lactobacterium grave* var. *cerasi*, *Lactobacterium listeri* var. *cerasi*, *Streptococcus cerasi* nov. sp. These species are fully described.

F. W. TANNER

Action of yeast types isolated from butter on the constituents of milk (SANDBLIN)  
12. Influence of H-ion concentration on the development of yeast and bacteria and on the development of beer (LAER) 16.

**Separating microorganisms from liquids.** W. HENNEBERG. *Brit.* 188,724, July 16, 1921. Microorganisms are sepd. from liquids by the addn. of microorganisms having a flock-forming tendency, and which preferably have no deleterious action on the liquid or on the culture so sepd. The process is applied to the *manuf. of yeast*, to *pplg. and recovering bacteria cultures*, and to *clarifying beverages* such as beer, or other liquids. Inocuous flocking lactic-acid bacteria for use in air-yeast *manuf.* can be isolated from com. pressed "infected" yeast and cultivated in wort-agar in the Petri-bowl. In making yeast, this culture is sown and cultivated with the yeast, or added during cultivation. It causes the quant. pptn. of the yeast when ripening is complete and the air is cut off. It may also be added to the washing-water to cause a like sepn.

The pptd. yeast, mixed with the flocking microorganisms, can be used as starting-yeast for a further operation.

#### D—BOTANY

B. M. DUGGAR

**Effects of the method of desiccation on the carbohydrates of plant tissue.** KARL PAUL LINK AND W. E. TOTTINGHAM. *J. Am. Chem. Soc.* **45**, 439-47(1923).—Carbohydrate detns. were made on 5 types of fresh plant tissue (beet leaves, corn ears, corn stalks, corn seedlings, potato tubers) preserved by drying in different ways. The results indicate that a temp. of 98° should not be used in the drying when the sugar and starch contents are high. Temps. as low as 65° in an air current under atm. pressure can be safely used with tissues that can be dried rapidly but not with tissues that cannot readily be reduced to thin sections. A temp. of 80° in a vacuum is decidedly superior to 65° in a vacuum. With coarsely divided tissues, such as corn ears, 80° in a vacuum gives better results if the tissue is first autoclaved to inhibit enzymic and respiratory processes. Well ventilated ovens, especially those in which a large vol. of air is circulated over the tissue, permit of low drying temps. with min. changes of tissue compn. The alc. method of preservation gave the same analytical results for carbohydrates as drying at 80° in a vacuum in the case of beet leaves and corn ears. None of the methods of preservation mentioned above is recommended when sol. protein is to be detd. C. A. R.

**Chemotherapy of plant diseases.** E. RIEHM. *Z. angew. Chem.* **36**, 3-4(1923).—No new data. A discussion of the field of chemotherapy in plants, and a review of recent work. J. J. WILLAMAN

#### E—NUTRITION

PHILIP B. HAWK

NORMAL

**Influence of accessory foodstuffs on cell respiration.** P. GYÖRGY. *Jahrb. Kinderheilk.* **94**, 55-63(1921); *Physiol. Abstracts* **6**, 319.—Accessory substances from milk and vegetables have the property of increasing cell respiration in isolated cells. H. G.

**The supplementary protein value of peanut flour.** W. H. EDDY AND RENA S. ECKMAN. *J. Biol. Chem.* **55**, 119-29(1923); cf. *C. A.* **12**, 838; **14**, 3100.—“When the protein-supplementing power of peanut flour is compared with that of muscle protein by feeding rations so constituted as to contain only about 10% of protein, 6 to 7% of this protein being contributed by wheat flour and the rest by peanut flour or meat residue, resp., and when these rations are further supplemented with 3% butter fat, 4% salts and brought to nearly equal calorie value per g., the peanut flour proves slightly superior to the meat as a growth producer and markedly superior for promoting reproduction.” Rats were used and it was calcd. that an av. of 0.08 g. more protein was eaten each day by those receiving the peanut mixt. than by those receiving the meat mixt. I. G.

**The protein efficiency of combinations of cornmeal and certain other feeding stuffs, notably rice bran.** L. A. MAYNARD, F. M. FRONDA AND T. C. CHEN. *J. Biol. Chem.* **55**, 145-55(1923).—Rats weighing 60 g. were placed upon diets contg. 9% protein. The gain in wt. per g. of protein eaten during the next 12 weeks was, if the protein was furnished by corn meal,  $1.18 \pm 0.023$  g.; if by corn meal and *linseed oil meal*,  $1.21 \pm 0.052$  g.; if by corn meal and *cottonseed oil meal*,  $1.23 \pm 0.046$  g.; if by corn meal and *peanut oil meal*,  $1.46 \pm 0.052$  g.; if by corn meal and *soy bean oil meal*,  $1.76 \pm 0.046$  g.; if by corn meal and *rice bran*  $1.63 \pm 0.036$  g.; if by *peanut oil meal* alone,  $1.45 \pm 0.046$  g.; if by *rice bran* alone  $1.47 \pm 0.055$  g. Both peanut oil meal and rice bran were superior to corn meal but a mixt. of corn meal and rice bran was even better, indicating a mutually

supplementing action that was not apparent in the case of peanut oil meal and corn meal. Data for soy bean oil meal alone were not obtained, so no conclusion can be drawn regarding a possible supplementary action.

I. GREENWALD

**Studies on carbohydrate metabolism. I. Some comparisons of blood sugar concentrations in venous blood and in finger blood.** G. L. FOSTER. *J. Biol. Chem.* **55**, 291-301 (1923).—In 2 dogs, the concn. of sugar (Folin-Wu method) in the capillary blood drawn from the foot was 208 and 203 mg. per 100 cc. resp., that in blood from the femoral artery was 210 and 208 mg., that in the blood from the vein was 176 and 184 mg. Blood was also drawn from the veins and finger tips of several students. During fasting, the concns. of sugar in the venous and finger blood were very nearly the same. After the ingestion of 100-200 g. glucose, the concn. in the finger blood rose to much higher levels (0.174-0.214%) than in the venous blood (0.133-0.170%), the rise in the latter being checked sooner and at a lower level. The hypoglycemia which nearly always followed the rise was much more marked in the venous than in the finger blood, in which it often failed to appear. After the ingestion of 100 g. fructose, the rise in the concn. of sugar in finger blood was less (0.114-0.139%) than after glucose and the rise in the concn. in venous blood was short and frequently entirely missing. After 80-100 g. galactose, the concn. of sugar in the finger blood rose to 0.212-0.284% and that in the venous blood to 0.203-0.269%. The rise continued for nearly 3 hrs. instead of the 0.5 hr. with glucose. After feeding 70 and 100 g. starch, the curves were similar to those obtained after feeding glucose. After feeding with agar, there was no change in the concn. of sugar in venous or in finger blood. II. **An interpretation of the blood sugar phenomena following the ingestion of glucose.** *Ibid* 303-14.—In many cases, the concns. of sugar in finger and venous blood are increased to the same extent 0.5 hr. after the ingestion of glucose but the latter soon falls. The administration of a second dose of glucose after the concn. of sugar in the blood had returned to normal, or lower than normal levels, after the ingestion of glucose, usually had no effect on the concn. of blood sugar. The facts are believed to be best interpreted by the view that the ingestion of glucose in some way accelerates the glycogenic function and that this acceleration has a certain latent period. Cf. Bornstein and Holm (*C. A.* **16**, 2892). Fructose forms glycogen more readily than glucose and galactose does so less readily.

I. GREENWALD

**The intestinal flora of rats on a diet deficient in fat-soluble vitamin A.** FRANCES CREEKMUR. *J. Infectious Diseases* **31**, 461-7 (1922).—There was a change in the relative proportions of Gram negative and Gram positive bacteria in the feces of rats fed with diets deficient in fat-sol. vitamin A. The feces of rats on the deficient diet were dry and hard and probably accounted for the disappearance of streptococci noticed. There was no change in the proportion of bacteria which fermented glucose, lactose and saccharose. The proportion of H<sub>2</sub>S-forming bacteria remained const. J. H. L.

**The antiscorbutic value of sterilized lemon juice and the question of the doses of antiscorbutic necessary in metabolism.** G. MOURIGUAND AND P. MICHEL. *Compt. rend. soc. biol.* **87**, 1403-4 (1922).—Expts. made with lemon juice heated 1½ hrs. at 120° show that it takes 30 to 40 cc. of the sterilized juice to prevent the development of scurvy in guinea pigs for the same length of time as it would be prevented by 2-3 cc. of fresh juice. The time which is required for the scurvy to develop varies according to the amt. of the juice administered daily. These expts. are thought to indicate that the antiscorbutic substance does not act as a catalyzer, but as a simple food.

S. MORGULIS

**Non-antiscorbutic adjuvants to the antiscorbutic substances.** G. MOURIGUAND AND P. MICHEL. *Compt. rend. soc. biol.* **87**, 1404-7 (1922).—Expts. were performed which show that hay which by itself is not antiscorbutic can augment the feeble anti-



scorbutic power of sterilized lemon juice, and transform a defective diet of oats into a non-defective one. It is assumed that the alimentary equil. is seriously upset through the absence of many indispensable substances, and the lack of such a sp. substance as the antiscorbutic readily becomes a menace under such circumstances. When, however, these various substances, upon the presence of which the alimentary equil. depends, are added to the diet a deficiency of the antiscorbutic is less serious either because the conditions in the intestine are more favorable for its action or because the organism's actual need for this substance is less.

S. MORGULIS

**The relation of avitaminosis to wound healing.** B. ISHIDO. *Arch. path. Anat.* (Virchow's) **240**, 241-8(1922).—Wound healing is delayed in guinea pigs and rats on a diet deficient in vitamins, such as oats and water or polished rice and water and salts. The susceptibility to infection is increased.

E. R. LONG

GAMBERINI, CARLO. Sul contenuto dell'acido solfidrico nelle feci umane in rapporto all'alimentazione. Bologna: N. Zanichelli. 34 pp. L. 6.

## F—PHYSIOLOGY

ANDREW HUNTER

**The importance of the kidney for the synthesis of hippuric acid in men, dogs, pigs and sheep.** I. SNAPPER, A. GRÜNBAUM AND J. NEUBERG. *Nederland. Tijdschr. Geneeskunde* **66**, I, 426-33(1922).—The statement of Bunge and Schmiedeberg (*Arch. exp. Path. Pharm.* **6**, 1876) that hippuric acid is formed in the kidney of a dog but not in other tissues of the animal is confirmed by extensive expts. in contradiction to the statement of Kinsbury and Bell (*C. A.* **9**, 2397) that all tissues may form hippuric acid. In other animals, however, the formation of hippuric acid may take part in all tissues. With human kidneys (extirpated in pathological cases) the formation of hippuric acid can be proved, also.

R. BEUTNER

**Nature of amylase in large intestine.** E. BIANCHI. *Arch. mal. Pappar. dig. nutrit.* **11**, 122-5(1921); *Physiol. Abstracts* **7**, 113.—The diminution of amylolytic activity in the feces which show a strong tryptic activity appears to be dependent on the occurrence of putrefaction.

H. G.

**Blood coagulation.** V. R. CERUTI. *Biochim. terap. speriment.* **8**, 237-40(1921); *Physiol. Abstracts* **7**, 103.—The work of Bordet, from which he concludes that thrombin is formed by the interaction of cytozyme and serozyme, the latter existing as a precursor in the blood, is quoted. C. shows that in hemophilia, and after the introduction of an anticoagulant into the circulation, and also during clotting, the serozyme content of the blood goes down, while the amt. of cytozyme is unaltered. On these grounds he differs from Bordet, and ascribes the fermentative clotting action to serozyme alone.

H. G.

**Oxidase reactions in the choroid plexus.** J. WATRIN. *Compt. rend. soc. biol.* **86**, 125-7(1922); *Physiol. Abstracts* **7**, 101.—Substances occur in the choroid plexus which give oxidase reactions. These substances, described as vesicular granulations when examd. by the test of Röhmann and Spitzer, are the same as the vesicular mitochondria seen by the method of Regaud or Benda.

H. G.

**The composition of the fat of infants.** A. BARDISIAN. *Pediatrics* **29**, 156-67(1921); *Physiol. Abstracts* **7**, 84.—Subcutaneous, mesenteric and perirenal fats from children of the age 3 months to 5 years were examd. chemically. Results show that subcutaneous fat has the highest content of oleic acid, and the highest calorific value. Mesenteric fat has less oleic acid, but more water-sol. fatty acid (butyric acid, etc.). Perirenal fat is intermediate. The fact is confirmed that the fat of sucklings contains less oleic and more water-sol. acid than that of older children.

H. G.

**Physiology of the perspiration.** R. PLAUT AND E. WILBRAND. *Z. Biol.* **74**, 191-

216(1922); *Physiol. Abstracts* 7, 125.—Generally the body can overcompensate, even during strong and continuous perspiration, the loss of water of the blood by that of the muscles. In cases of "Wärmestauung" or want of NaCl in the food, the change in water relationship may lead to a concn. of the hemoglobin. The warm-blooded organism can compensate this by reducing the consumption in other parts of the body. This counter-regulation outlasts the influence of the heat for several hrs., and may lead to a decrease of the temp. of the body. The  $\text{CO}_2$  eliminated from the perspiring and from the dry epidermis is the same. H. G.

**The rate of urea excretion. V. The effect of changes in blood urea concentration on the rate of urea excretion.** T. ADDIS AND D. R. DRURY. *J. Biol. Chem.* 55, 105-11 (1923).—In each of several expts., 2 men ingested a variable amt. of urea dissolved in 1000 cc.  $\text{H}_2\text{O}$  at about 6 A. M. and then drank about 500 cc.  $\text{H}_2\text{O}$  every hr. Beginning at least 3 hrs. after the ingestion of urea, the urine was collected in hourly periods and blood was taken exactly at the half-hr. With a variation in urea content in the blood of from 17.7 to 93.5 mg. per 100 cc., the ratio of urea in 1 hr.'s urine to urea in 100 cc. blood varied from 42.3 to 51.4, av. 46.1, standard deviation  $\pm 3.16$  in one subject and, in the other, from 50.0 to 61.2, av. 56.2, standard deviation  $\pm 2.68$  with a variation in blood urea concn. of from 20.2 to 108 mg. per 100 cc. **VI. The effect of very high blood urea concentrations on the rate of urea excretion.** D. R. DRURY. *Ibid* 113-8.—In rabbits, in which the concn. of urea in the blood was maintained at a high level by means of the continuous regular injection of urea, the ratio of urea in 1 hr.'s urine to urea in 100 cc. blood (collected at the mid-hour) was almost a const. even though the concn. in the blood rose to over 0.7%. The ratios obtained varied from about 3 to about 5. I. GREENWALD

**The effect of Eck fistula upon pancreatic diabetes in dogs.** B. M. HENDRIX AND J. E. SWERT. *J. Biol. Chem.* 55, 161-9(1923).—In Eck fistula pancreatectomized dogs, there is comparatively little glucose in the urine. After fasting, glucose may almost entirely disappear from the urine, although the concn. in the blood is from 0.2 to 0.3%. One dog received a subcutaneous injection of 10 g. glucose, which was followed by an increase in the urine of 15 g. glucose the next day and of 9 and 3 g. on the two following days. The fall in  $\text{CO}_2$ -combining power of the plasma was not so rapid in these animals as after simple pancreatectomy. Although there was no increase in the amino-acid N of the urine, it is believed that there was little or no formation of glucose from amino acids in these animals. It is suggested that the disturbances following the establishment of an Eck fistula may be due to a disturbance of carbohydrate, rather than of protein, metabolism. I. GREENWALD

**The inorganic phosphorus of the serum and plasma of 91 normal adults as determined by the Bell and Doisy method.** EDWARD TOLSTOI. *J. Biol. Chem.* 55, 157-60 (1923).—Blood was drawn before breakfast. Some was treated with 0.2%  $\text{K}_2\text{C}_2\text{O}_4$  for sepn. of plasma and the rest was allowed to clot. The clot was broken after 1 hr. and, after an additional 2 hrs., the serum was sepd. by centrifuging. The modification of Denis and von Meysenbug (*C. A.* 16, 2340) was used. The values obtained with serum or plasma were practically identical and varied from 2.5 to 3.3 mg. P per 100 cc. I. GREENWALD

**The selective action of the kidney as regards the excretion of inorganic salts.** W. DENIS. *J. Biol. Chem.* 55, 171-81(1923).—"Expts. made on dogs and on rabbits in which  $\text{MgSO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{MgCl}_2$ , NaCl and  $\text{Na}_3\text{HPO}_4$  (10 cc. of 0.33 to 0.5 M soln. per kg. body wt.) were administered by the intestine and by intravenous injection, and the subsequent excretion of these salts followed by means of blood analysis, indicate a selective retention on the part of the kidney for the  $\text{SO}_4^{--}$  which in 1 case was found to accumulate in the serum to a value of 3200% of its initial concn." Cf. *C. A.* 17, 1665. I. GREENWALD

Investigations on the immediate effect of heavy exercise (stair-running) on some phases of circulation and respiration in normal individuals. I. Oxygen and carbon dioxide content of blood drawn from the cubital vein before and after exercise. CHRISTEN LUNDSGAARD AND EGGERT MÖLLER. *J. Biol. Chem.* 55, 315-21(1923).—"The O<sub>2</sub> and CO<sub>2</sub> contents of blood drawn from a cubital vein have been detd. in a series of normal individuals at rest and within 1 min. after heavy exercise. The exercise consisted of running up and down a flight of stairs 5 times. The muscles of the arms were not used. In 16 subjects the O<sub>2</sub> of the venous blood showed a decrease (8.14-16.34% unsatn.) far outside the variations found during rest. In 1 subject the figures for the O<sub>2</sub> content during rest and after exercise showed no difference. The CO<sub>2</sub> content showed only small variations. In some instances a decrease, in others a small increase was found."

I. GREENWALD

The hydrolysis of amides in the animal body. The comparative stability of surface-active homologs in relation to the mechanism of enzyme action. C. H. FISKE. *J. Biol. Chem.* 55, 191-220(1923).—"When equiv. doses of AcNH<sub>2</sub>, EtCONH<sub>2</sub>, PrCONH<sub>2</sub> and BuCONH<sub>2</sub> are given subcutaneously to fasting cats, the amt. of unchanged amide excreted in the urine diminishes progressively as the no. of C atoms increases. From this and other evidence (such as variations in diminution in rate of amide excretion, amt. of urea and NH<sub>3</sub> in the urine, etc.), it is concluded that the rate of hydrolysis of these amides in the body increases with the length of the paraffin chain. When hydrolyzed by acid, EtCONH<sub>2</sub> is slightly less stable than AcNH<sub>2</sub>, but PrCONH<sub>2</sub> and BuCONH<sub>2</sub> are much more stable than either of the others. In alk. soln. the order is just the reverse of that found in the body; *i. e.*, the stability increases with the mol. wt. Consideration of the literature on ester hydrolysis by lipase and on certain reactions in the animal body (the oxidation of alcs., fatty acids and ketones) shows that the rate of decompn. of surface-active homologs tends to increase with the number of C atoms, contrary to the general rule with ordinary reagents in true solp. Since the

that the prepigment is an *o*- or *p*-dihydroxybenzene deriv., and that melanin arises from the polymerization of quinonoids. Strong oxidation of melanin brings about the 3rd stage. A yellow pigment, which will not reduce  $\text{AgNO}_3$ , is formed. This pigment can be obtained by the action of  $\text{H}_2\text{O}_2$ . In the body it has been observed only in the skin lymph nodes. The 4th phase includes the colorless decompn. products of melanin. There is no sufficient ground for assuming the presence of oxidizing or other enzymes in the skin. Radiation with ultra-violet light leads to a primary pigmentation and secondary depigmentation, in which  $\text{H}_2\text{O}_2$  may be concerned.

E. R. LONG

**Endocrine organ preparations and adrenaline secretion.** B. TOKUMITSU. *Tokyo Med. News* No. 2292 (1922); *Japan Med. World* 3, 345(1923).—The cortical layer prepn. not only inhibits the adrenaline secretion but it produces a substance that neutralizes adrenaline. The infusion of the posterior lobe of the pituitary body inhibits the adrenaline secretion, but that of the anterior lobe enhances the secretion. M. F. MAVR

**Experimental investigation of the erythropoietic function of the hypophysis.** J. WATRIN. *Compt. rend. soc. biol.* 87, 907-8(1922); cf. *C. A.* 16, 3689.—The hypophysis exercises an erythropoietic function during pregnancy. To find out if the same function is displayed as a result of bleeding, guinea pigs were bled to various degrees and the hypophysis was examd. histologically. As a consequence of repeated and extensive bleeding the hematopoietic function was quite clearly awakened but not in the same degree as during pregnancy.

S. MORGULIS

**Gastric leucopenesis following the ingestion of starch.** M. LOEPER AND G. MARCHAL. *Compt. rend. soc. biol.* 87, 1172-3(1922).—The migration of leucocytes into the gastric cavity has been observed following the ingestion of peptone. The present expts. were made with starch paste (125 g. of a 1% soln.), the contents being removed at regular intervals from the stomach and examd. The examn. extended from 20 min. after the meal until 2.5 hrs. afterwards. The leucopenesis is very great: in a normal person it was 575 after 20 min. and reached a max. of 2225 at the end of 45 min. The cells are chiefly polymorphonuclear. The mononuclears constitute not more than 30% while the eosinophiles make up 5-6% of the total. The opinion is expressed that the leucocytes aid in the gastric digestion of proteins as well as of starch. S. MORGULIS

**The influence of certain irritating substances on gastric leucopenesis.** M. LOEPER AND G. MARCHAL. *Compt. rend. soc. biol.* 87, 1350-1(1922).—Vinegar, tea and a laxative drink cause a rapid leucopenesis into the gastric cavity, which is especially marked with the last named substance. The leucopenesis is not associated with gastric secretion as can be inferred from the fact that sugar alone inhibits the gastric secretion causing a strong leucopenic reaction, while tea alone produces a similar leucopenesis without at the same time repressing the gastric secretion. S. MORGULIS

**Reaction of the isolated snail heart to an increase in potassium.** H. CARDOT. *Compt. rend. soc. biol.* 87, 1193-4(1922).—When perfusion is made with a soln. contg. little or no K following perfusion with a soln. having much K, every second systole shows a gradual diminution in amplitude until it completely disappears, while the amplitude of the intermediate systole little by little increases. When the content of K in the perfusion liquid is increased there is at first a quick cessation of the rapid rhythm, but after a more or less protracted diastolic pause the activity of the ventricle suddenly starts up again and it beats slowly and strongly. S. MORGULIS

**The reality of the increase in the number of red cells at high altitudes.** J. J. ISQUIERDO. *Compt. rend. soc. biol.* 87, 1195-6(1922).—Both in men living at an altitude of 2240 m. in Mexico and in animals which have been brought to that altitude, after a prelim. period of acclimatization, the number of red cells is considerably higher than at the lower altitudes. The red-cell count is to all practical purposes similar in

the heart blood and blood taken from a vein. However, these studies, though very conclusive, still leave the question open as to whether one is dealing here with an actual increase in the total number of cells or simply with an increased number per unit vol.

S. MORGULIS

Glandular cycle of the epithelium of the dog oviducts. R. COURRIER AND H. GERLINGER. *Compt. rend. soc. biol.* 87, 1363-5(1922).

S. MORGULIS

The female sexual cycle in certain hibernating mammals. R. COURRIER. *Compt. rend. soc. biol.* 87, 1365-7(1922).—The preëstral period in bats lasts about 7 months. During that period the following phenomena take place: rut, active secretion of uterus and oviduct, hyperplasia and keratinization of the vaginal epithelium. While in mammals in general the occurrence of rut always coincides with the presence of ripe follicles in the ovaries, this is not the case in hibernating mammals like the bat. The hypothesis is advanced that rut is not associated with the filling of the follicular sac but with factors which appear in the ovaries months before the follicles mature in bats and in other mammals just at the time of the ripening of the follicles. S. MORGULIS

Glucose content of the plasma and of the whole blood. F. SCHMID. *Compt. rend. soc. biol.* 87, 1367-9(1922).—The examn. of both the whole blood and of the plasma in a number of patients with different diseases and in normal individuals shows that when sugar is taken on an empty stomach in the morning the sugar content of both the plasma and of the blood is practically the same. There is therefore a definite equil. between the corpuscles and the plasma.

S. MORGULIS

The work of the kidneys. Glucosuria. R. CARRACIDO. *Rev. sci.* 60, 537-40 (1922).—A theoretical discussion. Phlorhizin is believed to affect the oxidative powers of the renal cells. Glucosuria is regarded as resulting from a diminution of the intrarenal combustion of sugar.

S. MORGULIS

Studies on the total bile. I. The effects of operation, exercise, hot weather, relief of obstruction, intercurrent disease and other normal and pathological influences. PHILIP D. McMASTER, G. O. BROWN AND PEYTON ROUS. *J. Exptl. Med.* 37, 395-420 (1923).—The bile varied in amt. from 3.5 to 9.5 cc. per kg. of dog in 24 hrs. Vigorous exercise does not increase the quantity of bile. During hot weather this may sink greatly and during intercurrent diseases unassociated with jaundice the flow may almost cease. The bilirubin output remains nearly const. from day to day, though slow changes may occur which are synchronous with similar changes in the hemoglobin % of the circulating blood. The pigment concn. varies inversely as the fluid quantity. When the bile flow almost ceases the pigment concn. becomes very great. Other observations are reported. II. The relation of carbohydrates to the output of bile pigment. *Ibid* 421-6.—Carbohydrate feeding or injection produces often a temporary increase in the rate at which bilirubin is put forth in the bile, but none in the amt. of the pigment secreted day by day. There would appear to be no ground for the supposition that bilirubin is normally derived in part from the carbohydrate of the food.

C. J. WEST

EGGE, RICHARD. Vejledning til Brug ved fysiologisk-kemiske Ovelser paa Universitetets fysiologiske Laboratorium. Kopenhagen: M. P. Madsen. 136 pp. Kr 7.75.

HALDANE, J. S. Respiration. New Haven: Yale University Press. 427 pp. Reviewed in *Physiol. Abstracts* 7, 468(1922).

#### G—PATHOLOGY

H. GIDEON WELLS

A test of the colloid stability of serum in cases of toxin formation in the organism, particularly in active tuberculosis. J. V. DARÁNYI. *Deut. med. Wochschr.* 48, 553-4 (1922).

S. AMBERG

**Specific and non-specific formation of antibodies.** THORWALD MADSEN. *J. State Med.* 31, 51-73(1923).—Daily injection of 0.05 g. of the chlorides of Mn, Ni, Co, Zn and other metals into goats that had been previously immunized by sp. agents served to maintain the antibody content of the blood at a high level. Similar results were obtained with the horse immunized against diphtheria. The salts of Be, Mn, Ba, Pb, Zn were especially potent in stimulating antibody formation. Fe and the chlorides of the alkali metals had practically no action. It is suggested that antibody formation is a secreting process and that the action of the metals is in the nature of a catalytic effect on enzyme processes. F. A. CAJORI

**Acidosis and alkalosis.** OTTO FORGES. *Naturwissenschaften* 11, 70-3(1923).—A review. C. C. DAVIS

**Free uric acid and renal permeability.** M. P. WEIL AND C. O. GUILLAUMIN. *Compt. rend. soc. biol.* 86, 319-20(1922); *Physiol. Abstracts* 7, 136; cf. *C. A.* 16, 1614, 2178.—The cause of gout is not the increase in free uric acid, but that of the combined uric acid. H. G.

**Blood sugar standards. Normal and diabetic persons.** HORACE GRAY. *Arch. Intern. Med.* 31, 241-58(1923). II. In conditions neither normal nor diabetic. *Ibid* 250-62.—A discussion of the results obtained in 900 expts. involving 4000 detns. of blood sugar, taken from the literature without regard to differences in the method employed. I. GREENWALD

**A study of the inorganic constituents of the blood serum in nephritis.** W. DENIS. AND S. HOBSON. *J. Biol. Chem.* 55, 183-90(1923); cf. *C. A.* 17, 1661.—In 22 cases of nephritis and cardi-renal disease, the Na and Cl of the serum were markedly increased in only 4 cases, all of which had edema, the inorg. P was increased in 10 cases, while the inorg. S was increased in 11 cases out of the 17 examd. Mg and K remained more or less const. and Ca was decreased in 5 cases (out of 22). The retention of S may be as great as 30 times the normal of 0.5 mg. per 100 cc. Among the inorg. constituents, S seems to resemble, in difficulty of excretion, uric acid of the nitrogenous metabolites. I. GREENWALD

**Protein feeding and high blood pressure.** SOLOMON STROUSE AND SARAH R. KELMAN. *Arch. Intern. Med.* 31, 151-63(1923).—"In patients with hypertension and with slight or no impairment of renal function marked variations in blood pressure occur. Such variations bear no relation to the intake of protein food. In such cases no damage to renal function and no increase in non-protein N or urea N of the blood was found to follow protein feeding up to 150 g. daily. In 3 such cases strong stock soup and coffee given daily did not increase the blood pressure. In cases of frank progressive nephritis with hypertension, a diminution of protein intake sufficient markedly to lower the figures for blood non-protein N and urea did not cause lowering of the blood pressure." I. GREENWALD

**The hydrogen ion concentration of the blood in carcinoma. I. From the colorimetric determination of the blood dialyzate.** W. H. CHAMBERS. *J. Biol. Chem.* 55, 229-56(1923).—"The dialysis method was modified slightly to minimize the loss of CO<sub>2</sub>. The changes in  $pH$  and CO<sub>2</sub> tension of a NaHCO<sub>3</sub> soln. and the loss of CO<sub>2</sub> through the oil at different temps. were studied. The factors for correcting the readings to 20° were found to be, per degree,  $pH$  0.004 for the PO<sub>4</sub> standard and  $pH$  0.01 for the blood. The dialyzate of the venous blood of normal subjects had an av.  $pH$  of 7.31 at 20°, that of pathol. cases other than carcinoma averaged 7.36, while that of 45 cases of carcinoma averaged 7.31. This increased alkalinity could not be associated with the degree of anemia but did appear to correspond to the size and extent of tumor growth. II. From the carbon dioxide-bicarbonate ratio. W. H. CHAMBERS AND R. E. KLEINSCHMIDT. *Ibid* 257-90.—The venous CO<sub>2</sub> tensions were read from the

CO<sub>2</sub>-absorption curves which were plotted at the venous O<sub>2</sub> tension, or from those plotted from fully oxygenated blood with a correction for venous O<sub>2</sub> unsatn. The pH was calcd. from the CO<sub>2</sub>:HCO<sub>3</sub> ratio and the av. was found to be 7.29 in 12 normal bloods, 7.33 in 8 detns. on bloods from patients with diseases other than carcinoma and 7.34 in 23 detns. on bloods from patients with carcinoma. "The alkalosis of the dialyzate in carcinoma cases compared to normal blood is explained by Donnan's theory as due to an increase in non-diffusible anions in the plasma."

I. GREENWALD

**The etiology of acute intestinal intoxication in infants.** GLADYS L. BOYD. *J. Biol. Chem.* **55**, 297-301(1923).—The intestinal mucosa of children dying of acute intestinal intoxication was extd. in boiling 0.1% HCl, concd. and filtered through a Berkefeld filter. The exts. were toxic to kittens, young rabbits and mice but not guinea pigs. By Kutscher's method crystals supposed to be those of  $\beta$ -imidazoleylethylamine picrate, m. 235-44°, were obtained. These were not toxic but became so upon boiling for 2 or 3 hrs. in abs. EtOH. Stool exts. and systemic blood were only slightly toxic but 1.5 cc. doses of portal blood obtained at necropsy produced convulsive twitchings, drowsiness, anorexia and increase in number of stools in each of 2 guinea pigs.

I. GREENWALD

**Color analysis of urine. V. The urochromogen excretion in health and disease.** M. WEISS. *Biochem. Z.* **134**, 567-88(1923); cf. *C. A.* **17**, 1258.—The urochromogen excretion of healthy adults ranges from 0.04 to 0.08 g. per day. It is somewhat greater per kg. body wt. in children. This is probably due to the more active metabolism. In old persons it is somewhat less. It is increased in pregnancy. In renal disorders the excretion is markedly decreased or even is lacking. A decrease is also found in pneumonia. It is increased in tuberculosis, other infectious diseases, tumors and uncompensated cardiac insufficiency.

F. S. HAMMETT

**Changes in the composition of the blood produced by inhaling oxygen under pressure.** H. HULL AND L. V. FRIEDRICH. *Klin. Wochschr.* **2**, 69-72(1923).—Oxygen, under a pressure of 10 to 18 cm. H<sub>2</sub>O in excess of the atm. pressure, was administered, by mask, to normal subjects, diabetics and hypertonics for from 15 to 60 min. The blood was then examd. for glucose, hemoglobin, protein, chlorides and erythrocytes. There is a rapid and marked reduction in the concn. of all of these constituents, which indicates that the blood is dild. by fluid poured in or extd. from the surrounding tissues. The blood pressure in normal subjects changes very little; but in hypertonics there is a marked fall in blood pressure that persists for some time after the oxygen administration has been discontinued.

MILTON HANKE

**Blood sugar values in the course of cirrhosis of the liver and their relation to the resulting alimentary glucosuria.** A. CHAUFFARD, P. BRODIN AND ZIZINE. *Compt. rend. soc. biol.* **85**, 305-7(1921).—Hyperglucemia existed in 11 patients who were suffering from cirrhosis of the liver. When 150 g. of glucose were administered in the morning on the empty stomach, 10 of these patients showed distinct glucosuria. The marked portal hypertension and the stasis in the visceral veins probably check the action of the pancreas and thus produce the hyperglucemia.

JOSEPH S. HEPBURN

**Ambard's constant.** M. IDE. *Rev. med. Louvaine* **1921**, 33-41; *Physiol. Abstracts* **6**, 267-8.—Ambard's laws concerning the secretion of urea are inexact. His formula lacks value since it expresses only the variations in the blood uræa. Cf. following abstr.

JOSEPH S. HEPBURN

**Ambard's constant.** SCHILLING AND F. STOBARTS. *Le Scalpel* **49**, 1173-95 (1921); *Physiol. Abstracts* **7**, 48.—The objections of Ide (cf. preceding abstr.) are discussed; and study is made of the clinical applications of this const. J. S. H.

**Rate of sedimentation of the red blood corpuscles in puerperal septic processes.** A. MAHNERT AND K. HORNECK. *Arch. Gynäkol.* **116**, 383-90(1922).—The speed of

sedimentation of the red blood corpuscles is greater in puerperal sepsis than in normal childbirth. Under the influence of therapeutic measures, such as the injection of disargen and Pregl's iodine solution, changes in the speed of sedimentation are brought about, paralleling the clinical condition. As cholesterol is increased in the blood in puerperal sepsis, it is probable that the sedimentation of the red blood corpuscles is related to the cholesterol content of the blood.

HARRIET F. HOLMES

**The pigment question.** B. BRAHN AND M. SCHMIDTMANN. *Arch. path. Anat.* (Virchow's) **239**, 488-90(1922).—The brown pigment which may be extd. from myocardium which has undergone brown atrophy cannot be distinguished from melanin. The wide variation in published analyses of melanin indicates that this is not a single substance but a group with similar properties. The pigment of brown atrophy is, like melanin, Fe-free and contains S and  $P_2O_5$ . Its rather difficult soly. in alkali does not indicate a non-melanin nature, as melanin varies considerably in this respect, becoming decreasingly sol. with age. For the present, human endogenous pigments are to be divided into two classes, those derived from hemoglobin, and the autochthonous pigments or melanins.

E. R. LONG

**The so-called lipofuscin.** O. LUBARSCH. *Arch. path. Anat.* (Virchow's) **239**, 491-503(1922).—A critical review. The designation "lipofuscin" and the distinction of the substance designated from melanin is unwarranted. The evidence at hand indicates that lipofuscin is a mixt. of pigment and fat, not a decompn. product of fatty substances. It is true that physiol. melanin is formed in ectodermal cells. Lipofuscin is not limited to ectodermal cells, although it is found there chiefly. It is not known whether its rare occurrence in connective tissue is to be attributed to its formation or deposition there. L. distinguishes 3 endogenous pigments (1) the hemoglobinogenous, (2) the proteinogenous, including "lipofuscin," and (3) the lipidogenous, including only the true lipochromes.

E. R. LONG

**Iron reaction in malaria pigment.** EDMUND MAYER. *Arch. path. Anat.* (Virchow's) **240**, 117-26(1922).—Although the usual microchemical reactions do not show the presence of Fe in malaria pigment, Fe can be demonstrated by certain modifications in which it is brought gradually into soln. and made to react with reagents at the same time. This is achieved by staining sections with Berlin blue in which aq. HCl is replaced by 2-5% alc. HCl, in which the malaria pigment is slowly sol., or with the Hueck modification of the Turnbull-blue reaction. In this method the  $(NH_4)_2S$  is allowed to act until the pigment begins to dissolve. The use of these methods confirms Seyfarth's finding (Verhandl. d. deutsch. Path. Ges. Jena, 1921) of Fe in malaria parasites. The finding of blue halos indicates that the Fe split from the pigment diffuses to the boundaries of the pigment-contg. cells. Occasionally blue or green globules of malaria pigment are seen with this technic. Formalin pigment does not give the Fe reaction with this method, which can accordingly be used for differential diagnosis.

E. R. LONG

**The phosphorus content of pathological melanin.** E. SALKOWSKI. *Arch. path. Anat.* (Virchow's) **240**, 353-5(1922).—Melanin from melanotic livers contained 0.99% and 0.71% P in 2 cases. P was found in the qual. examn. of another melanotic-liver melanin. Brown pigment from a brown, atrophied heart contained 0.18% P. The significance of this small amt. with respect to the nature of the pigment of the brown heart is doubtful. Other investigators have found a content of 0.50% P in the pigment of the brown heart.

E. R. LONG

**The preparation of bacterial antigens.** C. O. MELACK. *J. Med. Res.* **43**, 405-17 (1922).—Bacteria of the colon-typhoid group cultivated on non-protein media possessed the same antigenic value as organisms grown in protein-contg. media. For the prepn. of antigens entire cultures were frozen by immersion in liquid air and rapid thawing.



the process being repeated 20-25 times. The liquid was then centrifuged. The clear supernatant fluid so obtained has high antigenic value. The sediment contains little antigen and holds the bulk of the anticomplementary substance. The antigen can be kept 3 yrs. with little deterioration if kept frozen in sealed tubes. E. R. LONG

**Sensitization experiments with the tubercle bacillus and its protein extracts.** M. I. SMITH. *J. Med. Res.* 43, 435-45(1922).—Comparison was made of the tuberculin reaction and the anaphylactic state of tuberculous guinea pigs as shown by the uterus strip method. No apparent relation was noted. Tuberculin itself was devoid of sensitizing property. General hypersensitiveness does not always exist in the course of infection; on the contrary the development of the anaphylactic state in exptl. infection appears to be conditional upon the parenteral introduction of tuberculo-protein coincident with infection. Whether general sensitization by the protein of the bacilli growing in the diseased animal occurs is questionable. E. R. LONG

**Diasstase in blood and urine as a measure of renal efficiency.** G. A. HARRISON AND R. D. LAWRENCE. *Lancet* 1923, I, 169-70.—Diasstase estn. is useful in confirmation of other renal efficiency tests, but only in severe cases. Its concn. in the blood plasma or serum is conveniently detd. by the method of Wohlgemuth. It is necessary to demonstrate retention in the blood before concluding that disease of the kidneys is responsible for diminished excretion of the enzyme. The concn. of the enzyme remains const. throughout the day. The normal value for blood lies between 3 and 10 units. E. R. LONG

**Glucose tolerance in chronic arthritis.** G. L. K. PRINGLE AND S. MILLER. *Lancet* 1923, I, 171-5.—A lowered glucose tolerance, roughly proportional to the activity of the disease, is present in a large majority of cases of arthritis and muscular fibrositis. The tolerance returns to normal with recovery, and especially rapidly when infective foci are removed. Where the tolerance is low and the infective focus cannot be found the prognosis is bad. E. R. LONG

**Stability of antibodies in erysipelas and swine-plague serums.** EUGEN HAIBACH. *Z. Immunitäts.* 35, 407-28(1923).—Refrigeration as ordinarily practiced preserves the antibody content of erysipelas and swine-plague serums satisfactorily. Infection of the serum by cocci and molds lowers its antibody content. A phenol content of 0.5% does not prevent infection. Complete freedom from contamination in the preparation should be demanded. E. R. LONG

**Serologic studies with the help of the Zeiss liquid interferometer.** W. BACHMANN. *Z. Immunitäts.* 35, 462-82(1923).—The pptn. of egg white by antisera, the agglutination of bacteria by homologous serums, anaphylatoxin formation from bacteria *in vitro*, the flocculation reactions of Sachs-Georgi and Meinicke, and the Dold reaction do not cause changes in the refraction of liquids measurable by the interferometer. Lipolysis caused by serum lipase on tributyrin likewise does not affect the refraction value. The action of saliva on starch soln., and of urease on urea, causes notable increase of refraction, while that of trypsin upon peptone causes slight but measurable change. The theory that the reactions of immunity may be purely physical processes gains ground by the failure of refractometric recognition of antigen removal. E. R. LONG

**The agglutinating action of serum fractions.** STEPHAN WENT. *Z. Immunitäts.* 35, 503-22(1923).—Agglutinins cannot be considered as globulins. They are not precipitable by all the methods which ppt. globulins. Globulins obtained by dialysis do not contain the agglutinins, while those obtained by pptn. with  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{MgSO}_4$  and  $\text{Na}_2\text{SO}_4$  do. Agglutinins are present in the globulin fraction only as the result of adsorption. The reaction of the medium and its salt content are important factors in adsorption. A medium free from acid and salts is unfavorable for adsorption. E. R. LONG

**Isolation and estimation of complement-fixing substances in syphilitic sera.** I. FRANZ SKROP. *Z. Immunitäts.* 35, 523-38(1923).—The complement-fixing substance in luetic serum cannot be isolated in either the protein or lipid fraction of the serum, and is, therefore, neither protein nor lipid. It is separable through cataphoresis of the serum, possesses a pronounced electropositive character, and is present in normal serum, although in low concn. The complement-fixation reaction is a physicochemical process.

E. R. LONG

**The action of extracts from sclerosed pancreas on dogs made diabetic through the extirpation of the pancreas.** E. GLEY. *Compt. rend. soc. biol.* 87, 1322-5(1922).—Priority claim.

S. MORGULIS

**A new sero-diagnostic method for cancer.** A. WILBOUCHEVITCH. *Compt. rend. soc. biol.* 87, 1339-41(1922).—The principle of the method is the formation of a ppt. with KI-I<sub>2</sub> in the presence of citric acid, which serum from cancerous individuals possesses in a marked degree. The following solns. are needed: physiol. saline 0.75%, 5% citric acid in 1% HCHO, KI-I<sub>2</sub> soln. contg. 1 g. I and 2 g. KI in 210 cc. H<sub>2</sub>O. To 2 cc. of the citric soln. 0.5 cc. serum is added, then 0.7 cc. of the I soln. A ppt. forms which in normal serum soon dissolves but with cancerous serums remains permanent. In 75% of the cases examd. the test was positive.

S. MORGULIS

**Mode of action of certain bacterial toxins.** DOYON. *Compt. rend. soc. biol.* 87, 1352-4(1922).—The tetanus and diphtheria bacilli do not produce toxins directly. The culture filtrate, commonly known as toxin, at first contains nothing but a non-toxic sol. substance capable of forming the toxin with the aid of the receptive organism. It is the latter, the organism into which the sol. products of the bacilli are injected, which is the true generator of the tetanus and diphtheria toxins. The secretory products of the tetanus and diphtheria bacilli are pathogenic by virtue of their enzymic activity and not because of their toxic properties. The incubation period is a real chemical phase intermediate between the introduction of the microbial products and the appearance of morbid symptoms.

S. MORGULIS

**Use of creatinine as a test for renal function.** R. H. MAJOR. *J. Am. Med. Assoc.* 80, 384-8(1923).—Tests were made with 10 normal controls, 24 cases of disease other than nephritis and 16 nephritics. In normal persons or those suffering from various diseases with no renal lesions, the intravenous injection of 0.5 g. of creatinine was followed by an increased excretion in 1 hr. amounting to 3 times that excreted during the hr. preceding the injection. The total excretion at the end of 2 hrs. was 5 times that of the preinjection hr. In chronic nephritis the kidney fails to respond in this manner and in the cases studied this increase was less than 50%. In a no. of these patients no increase was observed.

L. W. RIGGS

**Chemical changes in the blood of the dog after intestinal obstruction.** R. L. HADEN AND T. G. ORR. *J. Exptl. Med.* 37, 365-75(1923).—A study of the non-protein N, urea N, uric acid, creatinine, NH<sub>2</sub>-acid N, sugar and chlorides of the blood and the CO<sub>2</sub>-combining power of the plasma in normal dogs and in dogs after different types of intestinal obstruction is reported. Following ligation of the duodenum, with or without gastroenterostomy and ligation of the upper half of the ileum, a fall in chlorides and a rise in the non-protein N and urea N of the blood and in the CO<sub>2</sub>-combining power of the plasma occur. The fundamental change is a fall of chlorides followed by an alkalosis, the degree of the latter depending upon the rate of formation of carbonate, rate of excretion by the kidneys and extent of neutralization of the carbonate by acids formed during the intoxication. The fall in chlorides is probably due to the utilization of the Cl<sup>-</sup> in the course of the intoxication. The urea N is a good index of the protein destruction. Ligation of the ileum at the ileocecal valve is followed by little increase in N and no change in the chlorides or CO<sub>2</sub>-combining power of the plasma. The close

similarity of the blood findings in intestinal obstruction, acute lobar pneumonia and serum disease suggests that these widely different conditions may have a common chem. basis.

C. J. WEST

**Chemical changes in the blood of the dog after pyloric obstruction.** R. L. HADEN AND T. G. ORR. *J. Exptl. Med.* 37, 377-81(1923); cf. preceding abstr.—The observation that a fall in chlorides and a rise in  $\text{CO}_2$ -combining power of the plasma occur after pyloric obstruction, is confirmed. There is also a marked rise in the non-protein N of the blood, consisting mainly of urea and undetd. N. The fall in chlorides is not due to the loss of chlorides in the gastric juice. The Cl is probably bound somewhere in the process of protein destruction. There is a close relation between this and the fall in the chlorides. A study of tetany should include the protein metabolism as well as that of the inorg. salts, since it seems possible that the tetany is due to protein split-products and not to the alkalosis. The chem. changes following pyloric obstruction are essentially the same as those following high intestinal obstruction. C. J. WEST

#### H—PHARMACOLOGY

ALFRED N. RICHARDS

**Contribution to the study of the influence of adrenaline on the respiration.** J. BOUCKAERT. *Arch. néerland. physiol.* 7, 285-91(1922).—By injecting into a cat or a rabbit 1 or 2 mg. ergotoxine or 0.6 g. caffeine the vasoconstrictor actions of adrenaline are suspended without affecting the respiration. The direct action on the respiration of adrenaline (1 or 2 cc. 1:10000) can be observed, therefore, after these injections. After injecting ergotoxine into a cat, the adrenaline causes a diminishing of the respiration. After injecting caffeine into a rabbit adrenaline stops the respiration for a short time. The action of adrenaline does not simply depend on the vasoconstriction; it seems to be of a sp. nature and must be distinguished from the action on the sympathetic system.

R. BRUTNER

**Silver arspenamine and sulfoxylate in malaria.** K. SURBEK. *Geneeskund. Tijdschr. Nederland. Indië* 62, 741-5(1922).—After injections of 0.35-0.4 kg. neosilver arspenamine or 8-10 cc. sulfoxylate in malaria patients a considerable reduction of the number of gametes in the blood is observed; in more than 50% of the cases the gametes disappear permanently.

R. BRUTNER

**Toxic manifestations following the alkaline treatment of peptic ulcer.** L. I. HARDT AND A. B. RIVERS. *Arch. Intern. Med.* 55, 171-80(1923). I. GREENWALD

**Experimental acid poisoning. II. Respiratory exchange in experimental acid poisoning.** A. LOEWY AND E. MÜNZER. *Biochem. Z.* 134, 437-41(1923).—Confirmation of previous work (cf. *Arch. Anat. Physiol.* 1901, 81) that the administration of toxic doses of HCl causes lowering of blood alkalinity and disturbance of tissue respiration. The nature of the latter lies in a decreased  $\text{O}_2$  consumption and increased  $\text{CO}_2$  formation, and not in an inability of the  $\text{CO}_2$  formed in the tissues to be removed by the blood. III. **Does methanol poisoning produce acidosis?** *Ibid* 442-6.—Basing the investigation on the finding of Pohl (*Arch. exp. path. Pharm.* 31(1893)) that MeOH is partly oxidized to formic acid in the body a study was made of the  $\text{CO}_2$  dissociation curve in the blood after the administration of the alc. It was found that the course of the reaction, even when the most severe symptoms of MeOH poisoning were present, was not that of an acid poisoning.

F. S. HAMMETT

**The influence of the hydron concentration on the antiseptic action of sublimate.** G. JOACHIMOGLU. *Biochem. Z.* 134, 489-92(1923).—The antiseptic power of 1:600,000  $\text{HgCl}_2$  solns. in various hydron concns. obtained by the use of glycocoll and citrate buffers was studied. A  $\text{pH}$  from 5.0 to 6.6 affords the best medium for antiseptic activity.  $\text{pH}$  7.8 to 10.1 is unfavorable.

F. S. HAMMETT

**New experiments with Vaughan's crude soluble poison.** F. P. UNDERHILL and ROBERT KAPINOW. *J. Lab. Clin. Med.* 8, 289-300(1923).—Vaughan's crude sol. poison possesses for the rat a degree of toxicity similar to that for the guinea pig. Coagulated egg white employed in the formation of this sol. poison yields a prepn. of high toxicity. The division of the substance into toxic and non-toxic fractions is not uniformly sharp; the so-called non-toxic residue may possess distinctly poisonous properties. Modifying the period of heating radically alters the toxicity of the product; long heating decreases the toxicity of the "crude sol. poison" and increases that of the "non-toxic residue." Vaughan's crude sol. poison can be obtained from the so-called non-toxic residue by further treatment. The substances included under the term Crude Soluble Poison are products formed presumably by progressive hydrolytic change, rather than by a division of the protein mol. into a toxic and non-toxic portion.

E. R. LONG

**The influence of atropine on the effects produced by adrenaline on blood vessels.** NILS WHELAND. *Compt. rend. soc. biol.* 87, 774-6(1922).—Frogs were perfused with oxygenated serum through the aorta under const. pressure, the perfusate being collected as it flowed out at the posterior end of the animal. When adrenaline 1:50,000,000 was added a strong vasoconstriction was produced. A soln. of atropine 1:100,000 causes an imperceptible dilatation. If, however, adrenaline is administered after a prelim. atropinization for 3-15 min. it loses its power to produce vasoconstriction and instead causes now a distinct dilatation. Reverting now to the atropine soln. again produces a constriction. If the perfusion is made with normal salt soln. and the system washed about 20 min. adrenaline recovers its original ability to cause vasoconstriction. Also if the perfusing fluid is free from Ca adrenaline instead of constricting dilates the blood vessels and after prelim. atropinization it no longer causes either constriction or dilatation. These results are interpreted to signify that the atropine paralyzes the motor fibers of the sympathetic nervous system, the sympathetic supply of the vessels being regarded as made up of both motor (constrictor) and inhibitor (dilator) fibers. Normally adrenaline affects the motor fibers more strongly than the dilator fibers, but when the former have been paralyzed by the atropine only the dilator effect becomes manifest.

S. MORGULIS

**Optimum conditions for the absorption of adrenaline from the digestive tract.** ALFONS TRIAS and H. DORLENCOURT. *Compt. rend. soc. biol.* 87, 1189-90(1922).—The absorption of adrenaline administered to a dog by mouth has been studied by the degree of hyperglucemia induced by the dose. The more concd. the soln. of adrenaline the more it is absorbed, and with an increase in concn. of 20 times a five-fold increase in hyperglucemia is obtained. The osmotic pressure of the solvent is of importance; the greatest absorption is obtained when adrenaline is given in Ringer soln. The following conclusions are given with regard to the therapeutic usage of adrenaline: medication by stomach is legitimate as adrenaline is absorbed through that channel, but doses 5-10 times as great as those generally given intravenously should be used in a small vol. of about 10 cc. soln. made up preferably in Ringer soln. or in a physiol. serum.

S. MORGULIS

**The comparative action of leech extracts and of nucleic acids on the frog. The superiority of nucleic acids as anticoagulants.** DOYON. *Compt. rend. soc. biol.* 87, 1351-2(1922).—In the frog especially nucleic acids exercise a much stronger anticoagulating effect and with less injurious action than other substances. S. MORGULIS

**Sectioning of the splanchnic and adrenaline glucosuria in the frog.** CL. GAUTIER. *Compt. rend. soc. biol.* 87, 1400-1(1922).—Destruction of the ganglia and of the fibers of the splanchnic in the frog does not interfere with the production of adrenaline glucosuria. S. MORGULIS

**Action of eserine and adrenaline in vivo on the pupil of the frog eye.** CL. GAUTIER. *Compt. rend. soc. biol.* 87, 1402-3(1922).—Injections of eserine cause marked contraction of the pupils. Occasionally when the contraction occurred it was noted that the pupil quickly dilated if the animal had convulsions. The action of the eserine is overcome by adrenaline, which causes the pupil to dilate. If an injection of adrenaline is given after an eserine injection had produced the characteristic effect a measurable dilatation of the pupil could be demonstrated. On the other hand, if an injection of adrenaline is given before the eserine, the latter fails to cause the usual effect. S. MORGULIS

WINTERSTEIN. **La Narcosis.** Translated from German by J. Goyanes. Madrid: Calpe. 232 pp.

# I—ZOOLOGY

R. A. GORTNER

Small contributions to comparative physiology. I. The nitrogen-metabolism with the Holothuroidea. H. C. VAN DER HEYDE. *Arch. néerland. physiol.* 8, 112-7(1922).—*Thyone briareus* Lesueur, a dendrochirotic marine animal, contains a proteolytic enzyme; this is proved by hydrolyzing solns. of gelatin and of egg albumin by means of an ext. prepd. from that animal; amino acids could be traced by ninhydrin. The statement to the contrary by Cohnheim (*Z. physiol. Chem.* 33, 9(1901)) seems to contradict the facts. II. Resorption with echinoderms. *Ibid* 118-47.—After injecting various foodstuffs into the intestinal tract of living animals the products of decompn. can be detected in the celom. The blind ending parts of the intestines of asteroids are organs of resorption; they contain the same quantity of protease as the stomach of the animals. Dissolved monoses or amino acids injected into the echinoderms rapidly disappear owing to resorption by amebocytes. The velocity of the resorption is not proportional to the injected quantity of these substances. III. Do enzymes exist in the perivisceral liquid of echinoderms. *Ibid* 148-50.—The statement of Cohnheim that enzymes of digestion exist in the celom liquid of echinoderms is erroneous. This is due to mixing of that liquid with fragments of blood corpuscles. IV. The excretions in echinoderms. *Ibid* 151-9.—All organs of excretion in the echinoderms also have respiratory functions. The wandering cells, which are the chief excretory organs, have a positive chemotropism for  $O_2$ , which seems to be of importance for their function. Uric acid can be detected (according to the method of Folin and Wu) in the celom fluid of echinoderms; urea,  $NH_3$  and creatinine are not found. R. BEUTNER

Biological semipermeable coating of the skin of some halisotonic sea animals. M. C. DEKHUYZEN. *Nederland. Tijdschr. Geneeskunde* 65, II, 800-4(1921).—Expts. with *Phascolosoma vulgare* are described. The body wall behaves like a semipermeable membrane. R. BEUTNER

Vital resistance of still transparent young snakes (cieche) to loss of water. G. BUGLIA. *Arch. ital. biol.* 71, 8-14(1922).—The slower the loss of  $H_2O$ , and the nearer the mol. concn. of the liquid into which they are returned to that of their own tissues, the greater the % of snakes which survive partial desiccation. A. T. CAMERON

On the mechanism of self-regulation of the number of chromosomes in the amphibian egg in parthenogenesis resulting from puncture. R. HOVASSE. *Compt. rend. soc. biol.* 87, 899-901(1922). S. MORGULIS

Influence of the interior medium of tritons on their eggs. A. WEBER. *Compt. rend. soc. biol.* 87, 902-4(1922).—Largely zoological. S. MORGULIS

Is the nucleus indispensable in the regeneration of protozoa? BORIS SOKOLOFF. *Compt. rend. soc. biol.* 87, 1144-7(1922).—For the reestablishment of the body form and for partial regeneration the nucleus is not necessary. The most active element in these processes is the ectoplasm, of which even minute fragments have the power

of regeneration. The nucleus is simply needed in the metabolic processes of the cell and its absence causes a cessation of assimilation and provokes cytoplasmic disintegration. The chromidia apparently do not possess this ability and cannot therefore replace the nucleus.

S. MORGULIS

**The thyroid gland of amphibia at the time of metamorphosis.** ZORJA MAYER-OWNA. *Compt. rend. soc. biol.* 87, 1175-6(1922).—In view of the stimulating effect which thyroid feeding exercises on the metamorphosis M. studied the changes which the tadpole thyroid of various species of frogs undergo. The gland increases in vol. most rapidly during the metamorphosis and attains a max. size just at the close of the process as manifested by the shortening of the tail and of the intestines. The number of vesicles in the gland also increases and these become more elongated. The epithelium changes from flat to columnar, and the colloid loses its staining capacity. These are changes accompanying increased thyroid activity, and the thyroid of the frog at the time of metamorphosis resembles very closely that of man suffering from Basedow's disease.

S. MORGULIS

**The effects of ultra-violet light on pond snails (Limnaeus).** C. W. M. POYNTER AND A. MORITZ. *J. Exptl. Zool.* 37, 1-13(1923).—Individual resistance of the snail embryos was large; it increased with age. The cytoplasm of the cells was coagulated by the rays, the effect produced resembling heat coagulation. This coagulation is probably secondary to a chem. change brought about by the rays. The effects of the rays are cumulative and their action is directly proportional to the time they operate.

CHAS. H. RICHARDSON

**Physiological studies on Planaria. V. Oxygen consumption of pieces with respect to length, level and time after section.** L. H. HYMAN. *J. Exptl. Zool.* 37, 47-68 (1923).—Expts. on *P. dorotocephala* showed that section of the body increases O consumption in the portions of the body sectioned; the respiratory rate due to section is greater the shorter the piece of the body involved. O consumption of long body pieces is const. within 24 hrs. after section. Expts. demonstrated a gradient in the rate of O consumption along the axis of the 1st zooid of *Planaria*. These results confirm conclusions previously reached in the Hull Zool. Lab., Univ. Chicago.

C. H. R.

**Excystation of Colpoda cucullus. Some factors affecting excystation of Colpoda cucullus from its resting cysts.** J. H. BODINE. *J. Exptl. Zool.* 37, 115-25(1923).—Studies on excystation, i. e., the stages up to and including the emergence of active protozoa from their resting cysts, showed that both active and encysted *Colpoda* are more resistant to gradual than to const. high temps. They can withstand long periods of desiccation. For excystation, acids are toxic in the following order: Salicylic > butyric > oxalic,  $H_3PO_4$ , HCl,  $H_2SO_4$  > AcOH. The resistance of cysts to various compds. is as follows:  $CS_2$  > alc., acetone >  $C_6H_6$ , toluene >  $Et_2O$  > xylene >  $CHCl_3$  >  $CCl_4$ . Resistance to temp., chem. compds., etc., seems to increase with the increase in degree of desiccation.

CHAS. H. RICHARDSON

**Thyroid transplantation and anuran metamorphosis.** W. W. SWINGLE. *J. Exptl. Zool.* 37, 219-57(1923).—Tadpoles of *Rana catesbeiana* and *R. clamata* were largely used in these expts. Transplantation expts. showed that the thyroid app. differentiated very slowly and was physiologically inactive during the greater part of the time. There is an activator of thyroid development in anurans which is probably secreted by the anterior lobe of the pituitary gland. Some additional expts. with *R. sylvatica* larvae from which the thyroid and hypophysis had been removed indicated that 3,5-dibromotyrosine and tyrosine did not accelerate metamorphosis while 3,5-diiodotyrosine simulated the action of thyroid ext., although the latter is somewhat more rapid. These results will be reported more fully elsewhere. The conclusions reached from this and other studies are: (1) It is the I in the tyrosine mol. which is essential for anuran

metamorphosis. (2) Thyroidless and pituitaryless frog larvae can metamorphose if fed thyroid substance or very large quantities of elemental I along with normal food. Diiodotyrosine is superior to any form of elemental I. An org. I complex is apparently necessary for metamorphosis and when inorg. I is fed, it must enter into org. combination with the larval tissues or food. (3) Diiodotyrosine can take the place of the thyroid hormone while the other iodized proteins and amino acids apparently cannot. Mammals and anurans are probably not comparable in regard to their reactions to I, since in the former diiodotyrosine cannot be substituted for thyroid tissue. (4) Br cannot take the place of I.

CHAS. H. RICHARDSON

**Comparative toxicity of various acids for fish (Epinoches).** MISS FRANCES GUEY-LARD AND MARCEL DUVAL. *Compt. rend.* 175, 1243-5(1922).—This study was made principally on *Gasterosteus aculeatus* var. *leleus*. Acetic, propionic, lactic and phosphoric acids were severally used in distd. water prep'd. in glass vessels. The acidity was measured by colorimetric  $p_H$  detns. and consecutive test solns. generally varied by  $p_H = 0.2$ . To avoid changes in acid concn., the Na salt of the acid studied was added to make the soln. 0.02 *N* and act as a buffer. Each fish as taken from the aquarium was washed in distd. water and placed in 100 cc. of the acid to be tested. Toxicity was measured by the time of survival. In  $H_3PO_4$  with  $p_H$  ranging from 2.2 to 3.4 the time of survival ranged from 15 to 57 min.; at  $p_H = 4.0$  the time was 8 hrs. In lactic acid with  $p_H$  ranging from 2.8 to 3.8 the time was 12 to 65 min., at  $p_H = 4.0$ , 155 min., and at  $p_H = 4.4$ , 8 hrs. In AcOH with  $p_H$  4.0 to 5.0 the time was 11 to 125 min. and at  $p_H = 5.4$ , 7.2 hrs. In propionic acid with  $p_H = 4.3$  to 5.2 the time was 9 to 70 min. and at  $p_H = 5.8$ , 7.1 hrs.

L. W. RIGGS

**Maturation in vitro and the activation by puncture of the ovarian eggs of *Rana fusca* at the time of egg-laying.** H. BARTHELEMY. *Compt. rend.* 175, 1248-9(1922); cf. *C. A.* 16, 971.—Largely zoological.

L. W. RIGGS

**Study of the  $p_H$  at the arrest of division of the egg of the sea urchin.** F. VILÈS, J. DRAGOIU AND M. ROSE. *Compt. rend.* 176, 133-6(1923); cf. *C. A.* 17, 441; Gray, *C. A.* 16, 3345.—Eggs of *Paracentrotus lividus* Lk. normally fertilized in sea water and at the beginning of the lengthening of the spindle of the first division, were immersed in sea water adjusted to different concns. of  $p_H$  by the addition of HCl, and their development was observed along with that of suitable controls. With  $p_H$  values between 8.1 and about 6.0 the modifications were slight; at  $p_H$  near 4.0 or less division it was totally arrested. With  $p_H$  near 6.0 division, if it takes place, is slower and is characterized by the appearance of abnormal forms. The critical value for total inhibition of division at 18° is between 5.2 and 4.9.

L. W. RIGGS

**Cytologic results of the lowering of the exterior  $p_H$  upon the evolution of the egg of the sea urchin.** J. DRAGOIU, F. VILÈS AND M. ROSE. *Compt. rend.* 176, 409-11(1923); cf. preceding abstract.—Lowering the  $p_H$  of the exterior medium (1) retards the evolution of the egg, and disturbs the synchronism of the external division of the cytoplasm with the interior phenomena of the nucleus, (2) produces alterations of structure in the cytoplasm and nucleus, and (3) sets up the preliminaries, at least, of cytolysis.

L. W. RIGGS

**New researches on the poison of ants.** ROBERT STUMPER. *Compt. rend.* 176, 330-2(1923); cf. *C. A.* 16, 1258, 1623, 3714.—The amt. of  $HCO_2H$  in g. per 100 g. of ants averaged 2.2 in *Cataglyphis bicolor* (Tunis), 0.91 in *Camponotus ethiops* (Italy) and 3.3 in *Camponotus maculatus* (Tunis). Expts. showed that  $HCOOH$  was the only acid obtained from the distn. of the 3 genera: *Formica*, *Cataglyphis* and *Camponotus*.

L. W. RIGGS

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

**Food adulteration and its control in a large city.** R. O. BROOKS. *Spice Mill* 46, 512-5(1923).—The duties and operation of a municipal food inspection department are outlined. Sophistications detected in 117 foods are listed. C. W. TRIGG

**Efficiency of some common anti-ferments. II.** E. H. HARVEY. *Am. J. Pharm.* 90, 105-8(1923); cf. *C. A.* 17, 1106.—The use of the oils of spices within the limits set by the taste is an aid in the preservation of such food products as catchup, tomato sauces, etc. Yeast is quite tolerant of salt solns. Saccharin exerts a mild anti-fermentative action, the quantity permissible in use being regulated by the taste. Dil. acid hydrolysis of sugar at room temp. gives data, which on plotting, produce a curve having the characteristics of enzyme-inverted sugar solns. W. G. GAESSLER

**Investigation of a technical separation of grits and flour for tariff classification.** J. BUCHWALD. *Z. Ges. Getriedew.* 14, No. 5-6, 45-58(1922).—Screening methods were used to sep. flour from grits, products of the flour being duty-free under the present tariff. 50-g. samples of the product to be tested were placed on a No. 3 screen, 23 mesh to 57 cm. and sifted about three minutes or until sifting was complete. The residue was weighed and results of the part passing the screen and residue expressed as percent of total sample. For wheat flour 75% must pass the screen, for corn meal 50%, and for rice food flour 25%. Results on domestic and foreign milling products showed the following to be classed as flour: wheat flour, hard wheat grits, corn meal, fine cream meal (corn), rice powder, rice food flour with powder. The following are classed as grits: Soft wheat grits, American hard wheat middlings, corn grits, cream meal (corn) and rice food flour without powder. F. A. CAJORI

**The influence of moisture content on the ash value of flour.** S. J. LAWELLIN. *National Miller* 28, No. 1(1923).—The ash content of any particular flour is inversely proportional to the moisture content. RUTH BUCHANAN

**Pasteurization of milk.** JOSEPH RACE. *Chemistry & Industry* 42, 166-9(1923).—Review. F. H.

**Physical and chemical changes of milk during pasteurization.** A. F. WEINIG. *Forsch. Geb. Milchwirtsch. u. Molkereiwes.* 2, 127-69, 175-205(1922).—Equal quantities of milk were heated in round-bottomed flasks of 3 l. capacity, so that 800 cc. of milk finally remained. The heating was carried out on the water bath with occasional careful shaking. The time taken to warm up and cool down was not reckoned in the time of pasteurization. The temps. used were between 60° and 80°. Careful pasteurization accelerates the sepn. of cream, but if a certain temp. is exceeded the sepn. is delayed. This critical temp. depends on duration of heating. If the milk is only heated for a few seconds the critical temp. may be above 75°, but if the duration of heating is 1/2 hr. the critical temp. is 63-4°. In judging the rate of sepn. in addn. to the amt. of cream sepg. in 24 hrs., the fat content of the cream should also be detd. The fat content of the cream sepg. in 24 hrs. is at first decreased by increasing the temp. of pasteurization, but does not usually fall as low as the value for raw milk. By further increase in the temp. of pasteurization it is again markedly increased. These changes in the creaming of the milk are primarily caused by changes in the compn. of the skin of albuminous colloid around the fat globules; the concn. and tenacity of this skin are increased by careful pasteurization, but considerably diminished at higher temps. The viscosity of milk is decreased by pasteurization at 60-5°, but less so by treatment at higher temps., and after treatment at 80° the viscosity usually exceeds the value for raw milk. The decrease is probably caused by changes in the casein, and the increase at higher temps. by vaporization of water, coupled perhaps with changes in the albumin. A definite



influence on the sp. gr. of milk could not be ascribed to pasteurization. The acidity of milk is reduced by pasteurization, but to different degrees in different samples. The albumin content of the milk is strongly influenced by the temp. and duration of pasteurization. By treatment at 60° for 1/2 hr. on an av. 8.5% of the sol. albumin becomes insol., but the amt. varies greatly from sample to sample. By treatment at 80° for 1 min. 40% of the sol. albumin became insol. The decompn. of the casein is illustrated by the altered behavior of milk on the addn. of rennet. Milk treated at 60° for 1/2 hr. has its coagulation by rennet delayed by 10.2%, while the time of coagulation of milk treated at 80° for 1 min. is increased by 32.6%. The changes in the casein are partly due to the pptn. of Ca and Mg salts. J. S. C. I.

**Cheddar cheese making.** J. P. GOW. *J. Dept. Agr. Union S. Africa* 6, 122-36 (1923).—A description of the process of manuf. of South African cheddar cheese. The common defects occurring in cheddar cheese are briefly discussed. K. D. JACOB

**Action of yeast types isolated from butter on the constituents of milk.** A. F. SANDELIN. *Ann. acad. sci. Fennicae* 19A, [3] (1922).—Various types of yeast isolated from butter (cf. *Ann. acad. sci. Fennicae* 12A, No. 6) were examd. with regard to their action on the various constituents of milk both when grown alone and in mixed cultures with *Streptococcus lactis*. All the yeasts used were *Torulae* according to Hansen's classification with one exception, which was a *Mycoderma*. The yeasts could be divided into groups according to their action on the constituents of milk. No type was found to act on all the constituents of milk—fat, sugar, and casein. J. S. C. I.

**The cause of explosion in chocolate candies.** JOHN WEINZIRL. *J. Bact.* 7, 599-604(1922).—Chocolate candies are subject to explosion due to the development of gas-forming microorganisms in them. Anaerobic bacteria of the type *B. sporogenes* are the chief cause but yeasts may also be a cause. *B. coli* is apparently not involved. The source of infection is usually the egg albumin. JOHN T. MEYERS

**The significance of amides in feeding stuffs.** F. HONCAMP. *Z. angew. Chem.* 36, 45-7(1923).—Cows fed on a low-protein ration utilized urea for both milk production and for storage in the body. As high as 200 g. per day per cow were without harmful effects. J. J. WILLAMAN

**Sunflower silage.** ANON. *J. Dept. Agr. Union S. Africa* 6, 116(1923).—Sunflower silage is somewhat inferior to corn silage and is not relished as much by animals. Its compn. is crude protein 1.24, carbohydrates 10.13, fat 0.37%; nutritive ratio 1 : 9.8. The sunflowers should be cut when about 50% in bloom. K. D. JACOB

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Changes in composition of beet leaves and tops stored in the field (WODARZ) 28.

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LUBLIN, JARL. **Margarinindustriens utvikling.** (The development of the margarine industry.) Stockholm. Reviewed in *Svensk Kem. Tids.* 34, 251(1922).

REITZ, ADOLF. **Nahrungsmittel und Fälscherkünste.** 4th Ed. Stuttgart: Francksche Verli. 88 pp. M 28.50.

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**Bread.** F. R. WARNER. U. S. 1,447,054, Feb. 27. A mixt. of malt ext. (contg. active diastase) 84, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> 6.5, monobasic Ca acid phosphate 6.5 and H<sub>3</sub>PO<sub>4</sub> 3% is used in prep. bread dough. This mixt. may be used in the amt. of 1% the wt. of the flour.

**Cocoa products.** N. H. DE GRAAF. U. S. 1,447,013, Feb. 27. Cocoa nibs or cocoa cakes are ground and at the same time mixed with coarse sugar and fluid milk while heating *in vacuo*. The product is then pulverized and kneaded with cacao butter. The resulting mixt. is adapted for use in beverages or confections.

**Ice cream.** L. H. P. MAYNARD. Brit. 189,026, Feb. 9, 1922. Lactic acid bacteria are added to condensed milk to produce an acid fermentation, a sep. mixt. of a material rich in butter fat, *e. g.*, fresh cream or cream made from butter, with sugar and an alkali such as CaO, is made, and the treated milk and cream are mixed to form the ice cream. The milk is first pasteurized at 165° F., then cooled and the bacteria are added. For slow fermentation a temp. of 32° F. may be used, and for rapid fermentation a temp. of 90° F.

**Apparatus for aerating milk.** J. M. W. KITCHEN. U. S. 1,447,249, Mar. 6.

**Aerating butter while melted.** J. M. W. KITCHEN. U. S. 1,447,250, Mar. 6.

**Modified pasteurized milk.** J. M. W. KITCHEN. U. S. 1,447,251, Mar. 6. The pat. relates to heating milk, modified for infant feeding, and pasteurizing it in bottles after freeing it from volatile putrefactive contaminants by a preliminary heating at about pasteurizing temp. or lower. U. S. 1,447,252 relates to a method of heating milk in bulk to purify it.

**Drying fruit by hot air blasts.** T. STRAWN. U. S. 1,447,493-4, Mar. 6.

**Fruit jelly.** H. T. LEO. Brit. 188,387, Aug. 8, 1921. A mixt. of pectous substances for a jelly base is produced by treating a material contg. pectose with a soln. of pectase derived from a non-acid vegetable, such as carrots. Acid present is removed by washing, or neutralized with CaCO<sub>3</sub>, and the pectous materials may be pptd. by alc. and dried by a blowing process.

**Food for animals.** J. BRAUNSCCHILD. Brit. 188,867, Sept. 30, 1921. Vegetable substances poor in starch and preferably those rich in cellulose are dried and comminuted and treated with a strong soln. of CaCl<sub>2</sub>. An increase in temp. follows, and a dry powder suitable for cattle, etc., food results. Suitable vegetable substances are mangolds, beet roots, carrots, cabbages, grass, fruit offal, spent grapes, straw, oat husks, and bran. The specification also refers to previous attempts to make dry-baking meal or flour by treating it with CaCl<sub>2</sub>, and sometimes by adding also fruit sugar or diastase.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

**Observations of industrial conditions in Europe.** W. S. LANDIS. *Ind. Eng. Chem.* 15, 410-2(1923). E. J. C.

**The work of the [British] patent office. Its functions and methods.** W. T. FRANKS. *Chem. Trade J.* 72, 163-5, 194-5(1923). E. J. C.

**Industrial potentialities of photosynthesis.** S. E. SHEPPARD. *Chem. Age* (N. Y.) 31, 57-61(1923). F. H.

**The technical investigation of adsorbents.** E. BERL AND K. ANDRESS. *Z. angew. Chem.* 35, 722-3(1922).—The relative powers of adsorbents may be estd. from the rise in temp. observed when 1.5 g. of the adsorbent is added to 10 g. of C<sub>4</sub>H<sub>6</sub> in an insulated test-tube. The adsorbing power decreases rapidly with increasing H<sub>2</sub>O content.

T. S. CARSWELL

**Safety in the compression of gases.** A. D. RISTERN. *Travelers Standard* 11, No. 1, 10-20(1923). E. J. C.

**Handling of corrosive gases in chemical plants.** C. S. ROBINSON. *Ind. Eng. Chem.* 15, 225-7(1923).—A summary of the requirements, and materials available, for the construction of blowers, fans and piping, used in the movement of corrosive gases at ordinary pressures. A. B. MARSHALL

**Chimneys subjected to acid gases.** T. S. CLARK. *Ind. Eng. Chem.* 15, 227-30(1923).—A review of the special conditions to be considered in designing chimneys for chem. and allied industrial plants. Effects of specific gases and fumes are discussed

and suitable methods of construction outlined. Details on the care and preservation of chimneys are given.

A. E. MARSHALL

**Preparation of pure gases by the application of the principle of the hydraulic compressor.** C. HEIRICH. *Z. kompr. u. fl. Gase* 22, 3-7, 21-2, 43-4(1922).—Where water power is available highly compressed gases can be most cheaply obtained by allowing the water to fall down a long vertical pipe, 300-400 m. high. Air or other gas is entrained with the water, sepd. at the bottom in a closed receiver under a pressure equal to the head of water, and the water allowed to pass away by an ascension pipe. By the use of flue gases in place of air the gases may be sepd. into  $\text{CO}_2$  and N in this app. It can also be applied to the purification of  $\text{SO}_2$ ,  $\text{NH}_3$ , and O, also of producer gas, etc.

J. S. C. I.

**Air humidity and drying.** P. H. PARR. *Intern. Sugar J.* 25, 16-20(1923).—Tables give for dry air the vol. and total heat per lb. and for satd. air the vapor wt., vol., total heat and heat increase per degree F. from  $40^\circ$  to  $100^\circ$ . By the use of these tables the amt. of heat required to dry a given wt. of sugar to any given moisture content can readily be ascertained.

W. L. OWEN

**Operating characteristics of flask evaporators.** JOHN FORBES. *Power Plant Eng.* 27, 311-3(1923).—High- and low-pressure and single- and double-effect evaporators are compared. High-pressure systems may be operated with live boiler steam where the amt. of make-up water is small, and low-pressure systems where exhaust steam is available and where it is advisable to supply an economizer for a low-temp. boiler feed heater. A single-effect system may be used where the auxiliaries are electrically driven and where the amt. of make-up water is small. If the amt. of make-up water is large a multiple-effect evaporator should be used. The flash evaporators are maintained under vacuum and the condensate is free from dissolved and entrained gases. Evapn. blow-downs are minimized.

G. C. BAKER

**Mask to aid in the artificial inhalation of oxygen.** RENÉ LEGENDRE AND MAURICE NICLOUX. *Compt. rend.* 176, 335-7(1923).

I. W. RIGGS

**Gran Enciclopedia de química industrial.** Barcelona: F. Seix. 96 pp. Pes. 7.

**Treating liquids with gases.** ALGEMEENE NORIT MAATSCHAPPIJ. *Brit.* 188,667, Nov. 10, 1922. The treatment is rendered more effective by carrying it out in the presence of activated C. The C is preferably obtained from vegetable raw material in such a manner that the structure of the raw material is retained. Powd. C may be mixed with the liquid and the mixt. then treated with the gas, preferably under pressure. Or the liquid and gas may be passed in countercurrent fashion through a column of granular C. Or the C may be caused to adsorb the gas and then used to treat the liquid. Such adsorption may be obtained by treating the C with gas under pressure at a low temp., or with a soln. of the gas in a portion of the liquid to be treated or in another liquid. The C may before use be treated to remove gases either by ignition or by heating in a vacuum. The process is applicable in bleaching liquids, in oxidizing drying and semi-drying oils, in the decompn. or oxidation of mineral oils for the purpose of converting them into fatty acids and other products, and in purifying and sterilizing  $\text{H}_2\text{O}$  or other liquids with Cl.

**Drying gases.** NITROGEN CORPORATION. *Brit.* 188,652, Oct. 31, 1922. In drying gases at a low pressure, e. g., N and H used in the manuf. of synthetic  $\text{NH}_3$ , the gases are passed through a chamber contg. hygroscopic material which on absorption of moisture is converted into a powder; this is removed from the chamber without the admission of air. A suitable construction is specified.

**Drying and separating gases.** ALGEMEENE NORIT MAATSCHAPPIJ. *Brit.* 188,666,

Nov. 10, 1922. A process of drying gases, or sepg. mixts. of gases, consists in treating them with active C, preferably of vegetable origin and dehydrated by ignition or by heating *in vacuo* before use, and in drying the gases or sepg. them by adsorption. *E. g.*, the gases are passed through containers filled with granules of active C and arranged in series so that as one container becomes exhausted it can be cut out of the series and the satd. C reactivated by heated inert gas, the inert gas being passed directly into the container, or into a perforated tube in the container with means for closing the perforations. The containers may be cooled to remove the heat of adsorption, the last containers of the series being cooled more than the first, and the cooled gas used for cooling the moist gas on the countercurrent principle. The drying is facilitated if the gas is compressed or its temp. reduced to about 0–5°. The process can be used to sep. light and heavy hydrocarbons, or to remove impurities such as hydrocarbons, CO<sub>2</sub>, etc., from H.

**Storing gases under pressure.** ALGEMEENE NORIT MAATSCHAPPIJ. Brit. 188,665, Nov. 10, 1922. Gases are stored under pressure in containers filled with active carbon, preferably of vegetable origin.

**Recovering vapors absorbed in porous materials.** E. R. SUTCLIFFE and H. S. RAPER. Brit. 188,723, July 17, 1921. Cases or vapors that have been absorbed by charcoal, etc., are recovered by treating the latter with superheated steam. After the removal of the absorbed gas or vapor, the passage of the superheated steam is continued in order to dry the absorbent substance; thereafter it is cooled, *e. g.*, by the passage of satd. steam to bring the absorbent substance into condition for immediate re-use.

**Filtration.** D. P. HYNES. Can. 228,736, Feb. 13, 1923. Pulp contg. solid and colloidal substances is prepd. for filtering by adding to the pulp, when substantially free from acid, a basic compd. of Zn to change the colloidal material to a form which does not inhibit filtration.

**Operating filters.** C. S. BRADLEY. Can. 228,782, Feb. 20, 1923. Pressure is applied within the interior of the filtering medium simultaneously and equally toward and away from its support, thus avoiding displacing tendency while passing fluid only through the filtering medium in a direction away from its support.

**Lubricants.** TECHNICAL RESEARCH WORKS, LTD. and R. G. PHELLY. Brit. 188,364, July 7, 1921. Derivs. of polyhydric alcs. or phenols, in which the hydroxyl groups are partially replaced by fatty or other acid radicals, are added to mineral oils or to saponifiable oils, fats, or waxes, to increase their lubricating and emulsifying properties, and to give them greater consistency. The monoglycerides of oleic and lauric acids may be used, and in an example, 5% of mono- or di-glyceride of oleic acid is added to a mineral lubricating oil.

**Lubricants; colloidal sulfur.** KEYSTONE OIL, & MANUFACTURING CO. Brit. 188,629, March 9, 1922. A lubricant especially adapted for screw-cutting, etc., machines consists of a colloidal soln. of S in mineral oil, preferably 5 lb. of S in 30 gal. of the product. It may be dild. with animal or vegetable oil or other liquid. In the preferred method of manuf., 5 lb. of finely divided brimstone are mixed cold with 1 qt. of "600" steam-refined cylinder oil to a smooth paste in a vat; the paste is added gradually from a container to 14–10 gal. of the same oil heated to above 195°, preferably about 220°, in a mixing kettle, and the mixt. is run slowly into 20 gal. of cold paraffin oil of 34° Bé. in a water-jacketed mixer. The mixer may be charged initially with several portions of paraffin oil and receive in succession the same no. of charges from the kettle.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

**Modern aspects of water purification.** R. J. S. McDOWALL. *Science Progress* 17, 325-7(1922).—Chlorination by means of bleaching powder is more economical than slow sand filtration and yields an equally satisfactory product. This method of chlorination was used by the British army in both the Egyptian and Mesopotamian campaigns.

JOSEPH S. HEPBURN

**The purification of drinking water for the (Italian) army during the war of 1915-18.** GIOVANNI GRIXONI. *Giorn. med. militare* 59, 283(1921); *Tech. sanit. munic.* 17, 18 (1922).—Br gave good results, but the supply did not last. The most widely used method was by means of NaOCl. Tincture of I is sure, but slower than NaOCl.  $\text{KMnO}_4$  was not found satisfactory.

A. P.-C.

**Emergency treatment of water for drinking purposes.** A. P. HITCHENS. *Military Surgeon* 51, 657-62(1922); *Pub. Health Eng. Absts.* Mar. 17, 1923.—Sufficient Ca(OCl)<sub>2</sub> is added to water in Lyster bags to produce an orange to orange-red color with o-tolidine. After 30 min. the excess Cl is neutralized with  $\text{Na}_2\text{S}_2\text{O}_5$ . G. C. BAKER

**Lead in drinking water.** C. D. HOWARD. *Am. J. Pub. Health* 13, 207(1923).—Experience has shown that lead poisoning may be caused by water contg. 0.25 p. p. m. Pb, although an arbitrary max. of 0.5 p. p. m. has been adopted. The use of Pb pipe seems more common in New England than the rest of the U. S. Details of a modification of the standard method for detn. of Pb are given.

JACK J. HINMAN, JR.

**The determination of hardness in technical waters.** FRANZ KANHÄUSER. *Chem.-Ztg.* 47, 57-9(1922).—Various sources of waters were investigated to find a suitable method for detg. the hardness. Special consideration was given to the effect of org. material. The Blacher method is recommended: det. alky. in 100 cc. (dilin. is made in case the water is very hard) with 0.1 N HCl with Mc orange as an indicator; destroy the Mc orange color with Br water; remove  $\text{CO}_2$  and free halogens; add 0.5 cc. of a 4% alc. phenolphthalein soln. and titrate with carbonate-free 0.1 N NaOH; remove the color with 0.1 N HCl and titrate the colorless liquid immediately with 0.1 N K palmitate. The hardness in German degrees is calcd. by multiplying the palmitate used by 2.8. If N/28 palmitate soln. is used the cc. of soln. used gives the degrees hardness directly. Fe and Mn do not interfere as they are pptd. as the hydroxides at the phenolphthalein neutral point. The Clark soap method gives low results for waters contg. org. material. In using the soap method on heavily contaminated waters, it is recommended that the water be evapd., the residue baked and brought into soln. with acid. The Blacher method gives good results for waters of high org. content, but if the water is highly colored it may be necessary to remove the color by adding Br water or evapn. with a few drops of aqua regia if it interferes with the phenolphthalein titration. The palmitate soln. may also be used to det. the  $\text{SO}_4$  content volumetrically as follows: ppt. the  $\text{SO}_4$  in the phenolphthalein-neutral and  $\text{CO}_2$ -free water with an excess of 0.1 N  $\text{BaCl}_2$ ; back-titrate this excess and total hardness with palmitate soln.; from the amt. of palmitate previously used for the hardness detn., the  $\text{SO}_4$  content is calcd.

H. D. CARTER

**Sterilization of small volumes of water by means of ozone.** S. BRÜGGE. *Tech. sanit. munic.* 17, 268-70(1922); cf. C. A. 16, 1628.—Two types of Van der Made sterilizers designed for treating 30 and 150 l. per hr. are described. The water automatically draws the requisite amt. of ozonized air and the mixt. passes upwards through a column having three horizontal celluloid partitions perforated with 0.6 mm. holes, which cause intimate contact of the water and gas. The smaller type absorbs 25 w. at 6,000 v. and the excess of ozonized air is allowed to escape. In the 150-l. type (which absorbs 30 w.) the excess of ozonized air is passed through a  $\text{CaCl}_2$  dehydrator and returns to

the ozonizer. The elec. current is automatically cut off or turned on with the water. A test of the 30-l. app. showed a reduction from 2,716 bacteria per cc. (including *B. coli communis* and putrefactive bacteria) to 2 of *B. subtilis*, and the 150-l. type a reduction from 2,345 per cc. to 8 of *Mucor mucedo* and *B. subtilis*. A. P.-C.

**Drinking water in factories.** H. MAMY. *Tech. sanit. munic.* 17, 2-6(1922).—Filtration, chem. treatment ( $\text{KMnO}_4$ ,  $\text{Cl}$ , I) heat,  $\text{O}_3$ , and ultra-violet rays are discussed. A. P.-C.

**The colloidal state and its relation to the filtration of drinking water and the purification of waste waters.** PAUL RAZOUS. *Industrie chimique* 10, 57-60(1923).—The effects of surface tension, elec. charges of the particles, and viscosity of the medium on the persistence of suspensions, and of the application of these principles to the coagulation and filtration of water are outlined. A. P.-C.

**Mineral waters in 1921.** W. D. COLLINS. U. S. Geol. Survey, *Mineral Resources of U. S.*, 1921, Part II, 229-36(preprint No. 29, published Feb. 5, 1923). E. H.

**A new artificial zeolite.** ANON. *Chem. Met. Eng.* 27, 1211(1922).—A satisfactory artificial zeolite, Doucil, British patents Nos. 142,974 and 177,746, is described. Two types of product are manufd. One is suitable for drying air and recovering solvent vapors; the other more suitable for water softening and purification. It is prepd. by intimately mixing at a temp. below  $20^\circ$  a dil. soln. of  $\text{Na}_2\text{AlO}_3$  and neutral  $\text{Na}_2\text{SiO}_3$ . The product contains 6 to 16% of  $\text{Al}_2\text{O}_3$  depending upon the total solids originally present in the mixture, and strength of soln. and final moisture content. 1 ft.<sup>3</sup> will soften 1000 gal. of  $\text{H}_2\text{O}$  contg. 10 parts  $\text{CaO}$  per 100,000. 4 lbs. of  $\text{NaCl}$  per ft.<sup>3</sup> of material is required for regeneration. It is guaranteed that 5% of the dry weight of the material can be exchanged for  $\text{Ca}$  compds. Exptl. work gives values of 7 to 8%. H. D. C.

**The "dionic water tester."** BOUSQUET. *La nature* (Supplement) 45, No. 2549 (1923).—Description with diagrams and photograph of the app. of Digby and Biggs for detg. the cond. of waters. JACK J. HINMAN, JR.

**The new filtration plant of the Norfolk water-works.** D. A. DECKER. *American City* 28, No. 1, 25(1923). NATHAN VAN PATTEN

**Special features of recent filter-plant design.** PAUL HANSEN. *J. Am. Water Works Assoc.* 10, 236-42(1923).—See C. A. 17, 166. E. H.

**A new activated-sludge sewage-disposal plant in California.** C. W. KOINER. *American City* 28, No. 1, 47(1923). NATHAN VAN PATTEN

**How sanitation aids the public health.** R. P. WALSH. *Bull. Dept. of Health, City of N. Y.* 13, 31(1923). JACK J. HINMAN, JR.

**How sanitation aids the public health.** ALONZO BLAUVELT. *Bull. Dept. of Health, City of N. Y.* 13, 25-30(1923).—The water supply, sewage and garbage disposal, bathing establishments and swimming pools, stables, lodging houses, laundries and offensive trades are dealt with. JACK J. HINMAN, JR.

**The destruction of bacterial dust and the deodorization of gases.** F. BORDAS. *Tech. sanit. munic.* 17, 56-60(1922).—In elec. pptn. of dusts, if the positive electrode, instead of consisting of a continuous tube, consists of a spiral or of sep. rings, the particles, which are in a special vibratory state, will glide along the walls of the electrode and will come out through the spaces between the segments. Expts. were carried out with bacterial dust ( $\text{Ca}_3(\text{PO}_4)_2$  ground to about 0.001 mm., sterilized, and inoculated with a very dil. culture of *Micrococcus prodigiosus*) in which complete sterilization was obtained by elec. pptn. at 30,000 v., the action being due partly to the pptg. action of the current and partly to the formation of  $\text{O}_3$ . After a brief review of results of others on the bactericidal and deodorizing power of  $\text{O}_3$ , the results of the expts. are summarized: most of the odors due to fermentation of org. matter are completely destroyed by the  $\text{O}_3$  generated in elec. pptn. in a moist atm.; the air can be completely sterilized and de-

odorized by passing through an elec. precipitator; the excess of  $O_2$ , which would be injurious to the human organism, is eliminated by passing the purified gas over rubber.

A. P.-C.

**The use of hydrocyanic acid by public services for disinfection.** PAOLO ALMASIO. *Riv. ingegneria sanitaria edilizia moderna* 17, 97, 105(1921); *Tech. sanit. munic.* 17, 17(1922).—The results conform with those of Lutrario. This method of disinfection is advisable in buildings which can be properly closed up, but not in those old or improperly built from which the HCN can escape to neighboring dwellings.

A. P.-C.

**Danger of disinfection by means of hydrocyanic acid gas.** CARLO MARINI. *L'Igiene moderna* 14, 294(1921); *Techn. sanit. munic.* 17, 226(1922).

A. P.-C.

**Experiments on disinfection and on the destruction of rats by means of hydrocyanic acid.** LUIGI PIRAS. *L'Igiene Moderna* 15, 101, 129(1921); *Tech. sanit. munic.* 17, 16-7(1922).—Expts. were carried out in accordance with the regulations of the Italian General Board of Health and gave satisfactory results. If care is taken the gas does not escape and reaches all infected places. If there is at least one generator per room and the HCN concn. is 0.2933%, the method presents the following advantages over the Clayton process: It can be used anywhere, as it does not deteriorate articles with which it comes in contact; a short time is required; it is cheaper; the generators are simple; HCN has a relatively high diffusive and penetrative power; and the method is quite safe if precautions are taken. For destroying rats the HCN content of the air need only be 0.1257%. It possesses advantages over the  $CO$ ,  $SO_2$  and  $CO_2$  methods.

A. P.-C.

**Chloropicrin.** RANDIER. *Arch. méd. pharm. navales* 122, Jan.-Feb. 1922, 22 pp.; *Tech. sanit. munic.* 17, 226(1922).—A monograph covering chem. and physical properties, toxicity to living organisms, and a detailed description of its application to the disinfection of the Russian warship "Kronstadt" after serious cases of bubonic plague. A bibliography is given.

A. P.-C.

**Septic tanks and ankylostomiasis.** VAIL. *Indian J. Med. Sci.* 9, 806(1922); *Bull. Inst. Pasteur* 20, 744(1922); *Bull. mens. internat. office d'hyg. publ.* 15, 124(1923).—The eggs and larvae of the hookworm are not destroyed in the septic tank, even when enough  $Cl$  is added to kill *B. coli*. Septic-tank products should be used as fertilizers with caution in countries where the hookworm is common.

JACK J. HINMAN, JR.

Apparatus for carbonating water or other liquids (U. S. pat. 1,447,884) 1.

**Preventing incrustation and corrosion.** E. R. JONES and W. S. SMITH. *Brit.* 188,778, Aug. 17, 1921. To prevent or reduce the corrosive or fouling action of  $H_2O$  on the walls of a boiler or on brass, Cu, Sn, rubber, glass, earthenware, etc. a mixt. of one or more sol. chlorides and one or more sol. chromates or dichromates is added to the  $H_2O$ . Na, K,  $NH_4$  or Zn chromate is preferably used.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

**Biochemical study of forest soils.** ANTONIN NĚMEC AND KVAPIL KAREL. *Compt. rend.* 176, 260-2(1923).—Tables are presented of detns. of the  $pH$  and catalytic activity of a number of Czechoslovakian soils under different conditions of forrestation. The  $pH$  of a given soil varies markedly with different species and forms of vegetation; in general the humus of deciduous timber shows a higher  $pH$  than that of evergreens of the same region. Soils bearing mixts. of deciduous and coniferous trees are less acid than those of purely deciduous or evergreen forests. The acidity of the humus and of the mineral

soil under the same species depends much, upon the nature of the soil considered.

P. R. DAWSON

**The chemical characteristics of clay and kaolin.** E. BLANCK AND W. GEILMANN. *J. Landw.* 70, 253-7(1922).—A report on the amt. of  $TiO_2$  in the soil, together with the method for *deig.*  $TiO_2$ . Kaolin contains an av. of 0.284% while clay contains an av. of 0.885%.

F. M. SCHERTZ

**The measurement of the acidity of soils by alkaline solutions.** V. VINCENT. *Compt. rend.* 175, 1233-4(1922).—The lower results given by solns. of  $NaHCO_3$  and  $Ca(HCO_3)_2$  as compared with  $Ca(OH)_2$  are explained by the non-reaction of the former with Fe and Si hydroxides as well as their less complete reaction with org. matter. Detn. of acidity by alkali bicarbonates gives only the org. acidity and that corresponding to salts of Al and of free alumina.

P. R. DAWSON

**Acid soils; employment of lime and ground chalk.** HENRI HITIER. *Bull. soc. agr. France* 1922, 289-93.—A discussion.

F. M. SCHERTZ

**Action of neutral salts on soils. Determination of soil acidity.** J. VAN DER SPEK. *Verslag. Land. Onderzoek. Rijkslandbouwproefsta.* 1922, 162-202.—A no. of acid and alk. soils were treated with various neutral salt solns. and the resulting H-ion concns. detd. electrometrically. Great differences in the effects of different salts were observed. That these effects are the outcome of adsorption phenomena, is indicated, by the different action of salts with the same anion or cation, and by the fact that the course of the reactions leading to the equil. position follows an adsorption isotherm. On the other hand, the equiv. interchange of cations and the course of reactions leading to the formation of substances of increased or decreased dissoc. in soln. favor the view that chem. reactions only are involved. Reactions occur between free ions in soln. and adsorbed ions. The different conceptions of the nature of chem. reactions in soils become simplified if it be assumed that adsorption of ions occurs on the surface of colloidal particles, and that adsorbed ions are not washed out by water but can still take part in reactions, and are interchangeable with ions bearing similar charges. In nature, acid solns., particularly  $H_2CO_3$  and humic acid, withdraw adsorbed basic ions from the soil leaving the free H-ions. The estn. of soil acidity by spotting out soil exts. on litmus paper is therefore inaccurate, since all the free H-ions are not extractable by water. The colorimetric estn. of soil acidity is best carried out with a salt-soln. soil ext., although results are unreliable unless standard conditions of concn. and quantity of soil and of extg. soln. are observed. Correct results can only be obtained by potentiometric methods.

J. S. C. I.

**The composition of Canton mud and Chinese fish-pond mud.** B. J. EATON AND C. D. V. GEORGI. *Malayan Agr. J.* 10, 238-9(1922).—These muds are used in the cultivation of potted plants.

E. H.

**The leaching of nitrate nitrogen and ammonia nitrogen from sand and loam soils.** W. GEILMANN. *J. Landw.* 70, 259-66(1922).— $NaNO_3$  and  $(NH_4)_2SO_4$  were used in expts. conducted in 4 leaching cylinders. With  $(NH_4)_2SO_4$  the crum structure of the loam remained unchanged, while with the  $NaNO_3$  the soil is tightly packed and difficult to work. The effect of the season is noted.

F. M. SCHERTZ

**Potato trials, 1922.** T. PARKER AND A. W. LONG. *Bull. Bur. Bio-tech.* 1, 259-61 (1923).—Six plots were treated with 5 cwt. per acre of sterilizer, spread broadcast and dug in 3 days after planting. The sterilizers were: A control, B 0.38% tar acids in crude base, C pure naphthalene, D 7.5% chlorophenols in crude base, E 2% org. hypochlorite in crude base, F 25% tar acids in crude base. The yields in lbs. per 100 lbs. of seed were, A 889, B 893, C 855, D 823, E 978, F 987. The treated plots produced larger tubers and were freer from disease, this being entirely absent in E and F. Analyses of the soils are given.

F. L. SEYMOUR-JONES



The improved Wiegner sedimentation apparatus. HERMANN GRESSNER. *Mit. Lebensm. Hyg.* 13, 238-43(1922).—The improvement is a device for making a continuous photographic record of the difference between the meniscus levels in the 2 tubes of the app. The device and resulting records are shown and the method of calcg. the % of particles of different size in the soil is explained. Cf. Wiegner, *C. A.* 14, 84; Odén, *C. A.* 14, 2116.

J. H. MOORE

Nitrogenous fertilizers. CAMILLE MATIGNON. *Progr. agr. vit.* 79, 137-40, 155-60, 208-13(1923).—An economic discussion of the present conditions of utilization and manuf. in France.

P. R. DAWSON

The effect of hexamethylenetetramine upon plant production. B. BLANCK, W. GEILMANN, AND F. GIESECKER. *J. Landw.* 70, 221-51(1922).— $(\text{CH}_2)_6\text{N}_4$  is formed as a condensation product from  $\text{NH}_3$  and  $\text{HCHO}$  as well as by the treatment of  $\text{NH}_3$ -contg. liquid manure with formalin. It is as favorable a source of N for the higher cultivated plants—oats, mustard and beets—as is  $(\text{NH}_4)_2\text{SO}_4$ . It is transformed by means of bacterial activity into  $\text{NH}_3$  and then into nitrate. The above facts were ascertained by means of pot expts.

F. M. SCHERTZ

Reduction of nitrates caused by seed as a possible factor in the economy of nitrogen in crop production. JERLEI DAVIDSON. *J. Am. Soc. Agron.* 14, 338-54(1922).—Reduction of nitrates is induced by seed under lab. conditions. Quantity of seed, basic radicals of the common nitrates, concn. of the nitrate soln. and the depth of the liquid in which the seed is submerged did not essentially affect the course of the process. At about  $50^\circ\text{F}$ . the reduction process was somewhat retarded. Growing seedlings produced a smaller quantity of nitrites than seed which had been devitalized by heating. Young seedlings induced reduction of nitrates when grown in soil. Seed devitalized by heating, as well as that naturally sterile, produced an appreciably larger quantity of nitrites than the growing seedlings under the same conditions. Actual loss of N was demonstrated as a result of reduction of nitrates by seed.

F. M. SCHERTZ

The basic-slag problem. C. F. JURITZ. *J. Dept. Agr. Union S. Africa* 6, 163-5 (1923); cf. *C. A.* 16, 4002.—High-grade basic slag, open-hearth basic slag and open-hearth fluorspar slag are briefly discussed and typical analyses given. The low availability of the  $\text{P}_2\text{O}_5$  in open-hearth fluorspar slag (6 to 50% of the total  $\text{P}_2\text{O}_5$ ) is particularly stressed. Typical analyses of 9 natural phosphates from different parts of the world are given.

K. D. JACOB

Protection of superphosphate sacks against corrosion. BRUNO. *Compt. rend. acad. agr. France* 8, 710-1(1922).—Sacks soaked in a marine algal soln. contg.  $\text{CaCO}_3$  in suspension exhibited a remarkable resistance to deterioration caused by acid phosphate. It is believed that the  $\text{CaCO}_3$  and the Ca pectate are able to neutralize the acidity, and produce inoffensive compds., as neutral calcium salts,  $\text{CO}_2$  and pectic materials. The cost of treatment is about 10 centimes per sack.

F. M. SCHERTZ

Lead arsenate and its preparation as an insecticide. PAUL MARCHAL. *Compt. rend. acad. agr. France* 8, 875-7(1922).—Arsenate prepd. from  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Na}_2\text{HAsO}_4$ , at a temp. below  $50^\circ$ , is very similar to pure lead arsenate. It remains in suspension rather long and possesses a superior adherence when compared with other arsenates of lead.

F. M. SCHERTZ

Studies on lime-sulfur (insecticidal) mixture. C. HARUKAWA. *Ber. Ohara Inst. landw. Forsch.* Japan 2, 1-20(1921).—Mixts. contg. lime and S in the proportions of 1:1 and 1:2, resp., were compared. Spraying expts. against scale insects showed no difference in effectiveness where quantities of the sprays contg. equal amts. of S were used. The reducing power towards  $\text{KMnO}_4$  solns. was the same with both sprays. It was noted that in all cases the amt. of  $\text{KMnO}_4$  reduced at ordinary temp. was  $1/2$  that reduced in boiling solns. Lime-S mixt. does not possess the power of dissolving the wax of the

scale insect. After death of the insect the activity of the oxidase and catalase of the tissue gradually decreases. Living as well as dead scale insects fall from infected trees after spraying with lime-S. The death of the insect may be judged by its change of color within a definite time after spraying. J. S. C. I.

**Controlling the strength of cattle dips.** ANON. *J. Dept. Agr. Union S. Africa* 6, 120(1923).—There are two sets of conditions where iodine "dip-testers" fail: (1) when the dip contains arsenate, which is not registered by the tester, and (2) when the test fluid has become weak through volatilization of the iodine. The testers should be occasionally checked up by chem. analysis. K. D. JACOB

**Spray spreading agents.** T. PARKER AND A. W. LONG. *Bull. Bur. Bio-tech.* 1, 252-8(1923).—Two sheets of glass of equal size were cleaned of grease, highly polished, and secured vertically. These were sprayed with solns. of lime sulfur 1 in 20,  $\text{NH}_4$  polysulfide 1 in 100, Pb arsenate 4 in 1000, liver of sulfur, and nicotine petroleum emulsion, with and without the addition of 0.2% Ca caseinate. In every case the caseinate greatly increased the wetting and penetrating power, making a far finer deposit. It greatly retards the settling of Pb arsenate from suspension. Expts. on various types of plants showed that it increased the insecticidal and fungicidal efficiency of some washes by 100%. F. L. SEYMOUR-JONES

**Researches on clothes-moth (*Tineola biselliella*, Hum).** E. TITSCHACK. *Z. tech. Biol.* 10, 1-168(1922).—A zoological study was carried out for F. Bayer u. Co. (cf. Ger. 347,723; *J. Soc. chem. Ind.* 41, 541 A) concerning the behavior of moth toward 52 materials, and also the influence of chem. reagents in gaseous, liquid and solid form, temp., light, moisture, reduced pressure and shaking on the eggs, larvae and moth. The results obtained with various chem. reagents are tabulated. J. S. C. I.

New bacillus for the fixation of nitrogen (TRUFFANT, BRZSSONOFF) 11C. Oxidation of sulfur by microorganisms (LIPMAN) 11C.

CIRO, RAVENNA: *Manuale di analisi chimica agraria e bromatologica*. 2nd Ed. Bologna: N. Zanichelli. 390 pp. L 28.

HUMMEL, HANS: *Der Stickstoff*. Stuttgart: E. Ulmer. 86 pp. M 60.

MAHIN, E. G. and CARR, R. H.: *Quantitative Agricultural Analysis*. New York: McGraw-Hill Book Co., Inc. 329 pp. \$2.75.

ZANNONI, ILARIO: *I concimi chimica nella pratica agricola, con speciale riguardo all' agro alessandrino e al Monferrato*. Casale Monferrato: Fratelli Torelli. 32 pp.

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

**The "amyl" process and its possible applications.** ERNST GALLE. *Z. angew. Chem.* 36, 17-9(1923).—The "amyl" process, whereby starch is fermented to  $\text{EtOH}$  by the mold *Amylomyces rouxii*, has never been adequately or accurately described (cf. Henneberg, *Praktikum* 365; Ost, *Chem. Technologie*; Maercker, *Handbuch*; Ullmann, *Enzyklopädie* I.), though recently new data have appeared (cf. Broun and MacPadyen, no reference; Lühder, *Z. Spiritusind.* 1914, 275; C. A. 16, 1830; Somlo, French patent 531,748). A detailed description is given of the process developed in recent yrs., in which maize is used as a source of starch, with the substitutes for maize developed during the war. C. C. DAVIS

**The direct transformation of amylaceous material into vinegar.** L. MANGIN. *Compt. rend. agr. France* 9, 134-6(1923).—The material is first cooked, then the starch is transformed into glucose by means of *Rhizopus*. Yeast is added to ferment the glucose

After filtration the alc. is converted to acid by bacteriol. means. Vinegar produced in this manner has a compn. very similar to vinegar from wine, and has an aroma due to the presence of esters and aldehydes which are lacking in vinegar obtained from pure alcohol.

F. M. SCHERTZ

**Standard methods of malt analysis.** Report of Standing Committee on Analysis, *J. Inst. Brewing* **28**, 775-86(1922).—In addition to the Seck lab. mill, a mill made by Messrs. R. Boby, Ltd., is now accepted as standard, and for grinding the grist a roller setting of 0.5 mm. is prescribed. In detg. the ext. of pale malts, the mash is kept at 150° F. for 1 hr., the practice of heating to 158° F. for the last 5 mins. being abandoned. The conditions of filtration of the worts are standardized; the first 50 cc. is to be returned to the funnel and 250 cc. finally collected. For reading the tint of worts any recognized "daylight" lamp may be used. Covered dishes are prescribed for moisture detns. and various precautions to be observed are enumerated. The "tube" method of estg. diastatic activity has been re-introduced as an official method, in addition to that previously given; and more exact details for the prepn. of sol. starch are laid down. No alterations have been made in the methods of analysis of colored malts and caramel.

J. S. C. I.

**Action of ultra-violet rays on fermentation and yeast.** P. LINDNER. *Woch. Brau.* **39**, 169-7(1922).—By using a bottom-fermentation brewery yeast, L. finds that the velocity of fermentation of dextrose is increased by the influence of ultra-violet light to even greater extent than was observed by R. and R. de Fazi (*C. A.* **10**, 950) in the case of top-fermentation beer yeast. Thus, fermentation of a soln. of 30 g. of dextrose in 300 cc. of water of 24 hrs. yielded 119 cc. of CO<sub>2</sub>, whereas when the fermenting liquid was exposed to the light of a mercury vapor lamp 2743 cc. of gas was evolved. The original yeast and that obtained from the latter soln. contained little glycogen, which was, however, present in large proportion in the yeast from the soln. not exposed to the ultra-violet light. Most of the yeast cells from the radiated solution were in active condition, about 20-30% being dead. Fermentation expts. with wort furnished similar results. Although exposure of yeast to ultra-violet light in a liquid fermenting under ordinary conditions favors the fermentation, exposure of the cells in a shallow layer of liquid to the light for any length of time produces fatal results.

J. S. C. I.

**Development and nutrition of yeast.** A. TAIT AND I. FLETCHER. *J. Inst. Brewing* **28**, 597-618(1922).—Fermentation expts. have been carried out at 65° F. and under varying conditions as regards amts. of seed yeast, nitrogenous nutrients, etc. Confirmation is obtained of A. J. Brown's observation that the quantity of new yeast formed is practically independent of the proportion of seed yeast used. The shape of the vessel employed exercises a marked influence in lab. fermentations. Abnormality has been encountered in expts. in which the nitrogenous pabulum of the yeast consisted of asparagine; growing yeast, in its search for nitrogenous food, breaks down asparagine with final production of malic acid, which acts as a poison and inhibits reproduction when its concn. attains a certain value. When, however, asparagine is used in conjunction with other amphoteric substances, it is possible for yeast to assimilate a greater proportion of N. The favorable influence exerted on the assimilation of N and the development of yeast by addn. of CaCO<sub>3</sub> to an asparagine medium is only slight, partly because of a mech. clogging of the yeast by the particles of carbonate with consequent diminution of the diffusion surface. Certain other substances, such as BaSO<sub>4</sub> and kaolin, exhibit a similar effect. Yeasts grown in presence of widely different proportions of nitrogenous compds. vary considerably in N content and the fermentative power varies approximately with the N content.

J. S. C. I.

**Hydrogen-ion concentration in the brewery.** IV. W. WINDISCH, W. DIETRICH, AND P. KOLBACH. *Woch. Brau.* **39**, 145-8, 151-3, 157-62, 165-6, 171-2, 177-9, 183-6

(1922); cf. C. A. 17, 609.—Details are given of a no. of investigations, by both the electrometric and the graphic titrimetric methods, of the titration acidity, H-ion concn., and buffer effect in worts and beers of various types. The essential result achieved is a proof that indications of sufficient accuracy for practical purposes are obtained if the rectilinear colorimetric titration curve is used in place of the  $p_H$  curve. J. S. C. I.

**Influence of hydrogen-ion concentration on the development of yeast and bacteria and on the stability of beer.** M. H. VAN LAER. *Petit J. Brasseur* 1922, Nos. 1193, 1194; *Woch. Brau.* 39, 226-7(1922).—In Pasteur's soln., contg. its nitrogenous nutriment in the form of  $NH_3$ , which is assimilable with difficulty by yeast, the latter exhibits its greatest multiplication at  $p_H$  6.8, i. e., in the neighborhood of abs. neutrality; in unhopped and hopped worts prepd. from 50% of malt and 50% of raw grain, however, the optimum values of  $p_H$  are 4.6 and 6.0, resp. Hence, the richer the liquid is in nutriment, the higher is the acidity which the yeast is able to withstand. If the culture soln. is not perfectly suited to the food requirements of the yeast, the latter is more sensitive towards increase of the alk. than towards increase of the acidity. For Froberg and for distillery yeast the optimum value of  $p_H$  is also 4.6, whereas for lambic yeast it is not higher than 3.8. For two of the most common disease organisms of Belgian beers, namely *Bacillus viscosus bruxellensis* and *Saccharobacillus*, the optimum values of  $p_H$  are, resp., 5.5 and 6.8. It is, therefore, evident, that, with unhopped wort, the optimum  $p_H$  for the disease organisms is nearer to the natural reaction of the wort than is that for yeast, while with hopped wort the reverse is the case. Moreover, when Froberg yeast and *Saccharobacillus* are sown together in hopped wort, the bacteria do not develop appreciably if the  $p_H$  of the liquid is below 5.4. Thus, the actual acidity of wort and beer constitutes an important factor in the stability, the highest infection being without results in a sufficiently acid wort. J. S. C. I.

**Fermentation accelerators.** INOUE. *Woch. Brau.* 39, 191-3(1922).—I. has repeated with Japanese bottom fermentation brewery yeast, both fresh and dried, and with the pressed juice prepd. therefrom, the expts. of Neuberg and his collaborators on the effect of certain aldehydes, ketones, diketones, disulfides, etc., on the velocity of the fermentation. The stimulating action observed is most marked with the pressed juice and least marked with the dried yeast. Contrary to Neuberg's result, vanillin is found to have a distinct, although slight, accelerating action on fermentation by yeast juice. With juglone, fenchone, and iron the effect is more pronounced. Neutral org. salts exert no action, although Von Euler and Casel observed activation by such compds. Shikimic, abietic and cholic acids cause slight activation. The fact that AcH effects permanent acceleration of fermentation supports Neuberg's scheme for the mechanism of fermentation. Xylose and uric acid also accelerate fermentation. J. S. C. I.

**The prevention of "ropiness" in beer from the practical point of view.** P. A. MASON. *Bull. Bur. Bio-tech.* 1, 238-43(1923); cf. Hampshire, C. A. 17, 178.—The use of liquid "finings," the base of which is pure lactic acid, inhibits the development of *Acetobacter R.*, which causes ropiness. Prevention of infection is discussed.

F. L. SEYMOUR-JONES

**Standard solution for the estimation of color in beers and worts.** B. LAMPE. *Woch. Brau.* 39, 235-6(1922).—A mixt. of solns. of  $Co(NO_3)_2$  and  $K_2Cr_2O_7$  is suggested as a standard. It has the advantage over the standards now in use—ferric alum, I, and aniline dye solns.—that it is stable for a considerable period and that the salts required can be obtained readily in a pure condition. J. S. C. I.

**An anomaly in the determination of volatile acids in wine.** J. ESTALELLA. *Anales soc. españ. fis. quim.* 20, 265-70(1922).—In the estn. of volatile acids in wine by distn. and neutralization with standard NaOH soln., phenolphthalein being used as an indicator, it is sometimes noticed that the neutral liquid becomes alk. on standing. This is attrib-

uted to  $\text{SO}_2$  in the distillate which is converted to  $\text{Na}_2\text{SO}_3$  and then reacts with any  $\text{AcH}$  present forming the usual bisulfite compd. and liberating  $\text{NaOH}$ . L. F. GILSON

**Estimation of unsaccharified starch in brewers' grains.** H. WÄSS. *Z. ges. Brauw.* 45, 122-4 (1922).—The following sedimentimetric method for the estn. of unsaccharified starch in brewers' grains yields accurate results in far less time than saccharification by means of diastase or malt ext. and subsequent detn. of the quantity of ext.; 10 g. of the wet grains is well triturated with 10 cc. of water in a porcelain casserole and then heated carefully to boiling during 10 minutes with 80 cc. of  $\text{CaCl}_2$  soln. (1 part of the anhyd. chloride and 1 part of water); if alk. to phenolphthalein, the  $\text{CaCl}_2$  soln. must be neutralized by addn. of  $\text{AcOH}$  before use. The contents of the casserole are transferred quantitatively by means of hot water to a 100 cc. flask, cooled, made up to vol., mixed, and filtered through a dry pleated filter paper. A starch soln. is also prepd. by heating 1 g. of barley (or wheat) starch, dried at  $100^\circ$ , with 10 cc. of water and 50 cc. of the  $\text{CaCl}_2$  soln. in a 100 cc. flask and afterwards treating in the same way as the wet grains. Of the two solns. thus obtained 10 cc. is mixed with 1 cc. of 0.5  $N$   $\text{I}$  soln. in two sedimentation tubes having the narrowed bottom portion graduated. After a short time the starch iodide should sep. out and the supernatant liquid should be, not colorless or blue, but distinctly yellow. The tubes are then centrifuged for 10 minutes at not less than 1200-1400 revolutions per minute, and the % of unsaccharified starch in the grains is calcd. from the vols. occupied by the starch iodide in the two cases. Where no suitable centrifuge is available, 10 cc. of the starch soln. from the grains is diluted in a 200 cc. cylinder with 100 cc. of water and the liquid treated with very dil.  $\text{I}$  soln. until the max. blue coloration is attained. The soln. of pure starch is treated similarly and the coloration of the one or the other liquid adjusted by dilution to equality with that of the other.

J. S. C. I.

Separating microorganisms from liquids (Brit. 188,724) 11C.

CIAPETTI, GINO: L'alcool industriale. Produzione ed applicazione dell' alcool alla forza motrice, alla illuminazione, alle industrie. 2nd Ed. revised and enlarged. Mailand: U. Hoepli. 275 pp. L. 10.50.

**Apparatus for comminuting and drying yeast.** E. KLEIN. U. S. 1,447,789, Mar. 6. The app. is adapted for comminuting compressed yeast in a drying chamber and for carrying the finely divided dried yeast particles from the comminuting and drying chamber to a settling chamber by the current of air employed for drying. Cf. C. A. 16, 2958.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**The industry of volatile citrus oils.** H. C. HOLTZ. *Chem. Weekblad* 18, 108-13, 362-7 (1921); cf. C. A. 15, 921.—Analytical data, constituents and phys. constns. for lemon, bergamot, mandarin, citron, lime and grapefruit oils are compiled from the literature. *Chinotto*, a little known oil obtained by distn. from the rind of *Citrus sinensis* Pers. is described;  $d_{20}^4$  0.847,  $[\alpha]_D^{25}$   $94^\circ 10' - 95^\circ 40'$ ,  $n_{20}^D$  1.47261, difficulty sol. in 80%  $\text{EtOH}$ , sol. in 4-4.5 parts 90%  $\text{EtOH}$ , contains 97-98% limonene, a small amt. of pinene and aldehydes. Numerous data are given on the cultivation of citrus trees, yields in oils, and statistics on production and export. The increasing importance of terpene-free citrus oils and their advantages for special purposes are discussed.

A. W. DOX

**Iodometric determination of antipyrine.** I. M. KOLTHOFF. *Pharm. Weekblad* 60, 194-9(1923).—A modification of the method of Bougault (*C. A.* 11, 2386) whereby NaOAc is substituted for NaHCO<sub>3</sub>, the time of reaction reduced to 20 min., and the excess I titrated in the presence of EtOH instead of CHCl<sub>3</sub>. To 10 cc. of a 1% antipyrine soln. add 1.5-2.0 g. NaOAc and 20 cc. 0.1 N I, stopper the flask and let stand 20 min. Add 20-25 cc. EtOH, shake until all the crystals are dissolved, and titrate the excess I with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. The method is applicable to the detn. of antipyrine in salipyrine and migraine, or in the presence of PhNHAc, phenacetin and aspirin. With pyramidone oxidation occurs with the development of a violet, then a red color. A. W. DOX

**Estimation of narcotine and papaverine in opium.** H. E. ANNETT AND M. N. BOSCH. *Analyst* 48, 53-8(1923).—The method, based on an observation by Plugge (*Arch. Pharm.* 25, 793) to the effect that on the addition of NaOAc to a soln. of opium alkaloids the only ones pptd. are papaverine, narcotine and narcine, is as follows: Rub up 1.5 g. of opium in a mortar with 4-5 cc. of 5% H<sub>2</sub>SO<sub>4</sub>, run in from a buret. Add more acid with continual stirring until the total amounts to 30 cc. Stir the mixt. with a pestle at intervals during 30 min., then filter. Heat an aliquot of 20 cc. (= 1 g. of the sample) in a small beaker to boiling on a H<sub>2</sub>O bath, and add 16 g. of NaOAc. Continue heating to complete soln. of the salt, mix thoroughly and let stand overnight. Filter and transfer the ppt. completely to the paper, and wash well with H<sub>2</sub>O. After drying both filter and ppt. in a H<sub>2</sub>O oven, powder the ppt. roughly by rubbing one side of the paper against the other; then ext. with hot PhMe, receiving it in a separatory funnel, 20 to 25 cc. in all being used. Now add 20 cc. of 10% NaOH soln. to the PhMe, and shake gently to ext. resinous and coloring matters from the PhMe soln. Reject the alk. soln. and wash twice with 20-cc. portions of H<sub>2</sub>O to remove all the NaOH. Evap. the PhMe to dryness in a weighed glass dish, finally adding 2 to 3 cc. of EtOH to facilitate crystn. Dry at 100° and weigh as narcotine and papaverine. Accurate results are claimed for the method, and it has the advantage that practically any wt. of opium may be taken for analysis, no correction factors being required. W. O. E.

**Development of the American arsphenamine industry.** G. W. RAIZISS. *Ind. Eng. Chem.* 15, 413-5(1923).—A resumé of the progress made in the manuf. and application of modern arsenicals, largely in the direction of venereal diseases. This remarkable development in chemotherapy has likewise been marked by the great impetus given to the elaboration of new chem. compds. for use in the treatment, not only of syphilis, but other diseases, as pneumonia, tuberculosis, leprosy, etc. W. O. E.

**Coöperation between chemist and perfumer.** H. J. PRINS. *Perfumery Essent. Oil Record* 14, 44-7(1923).—A discussion showing the necessity for and nature of close coöperation between chemist and perfumer, analogous to the relations existing between the manuf. of dyestuffs and the colorist. W. O. E.

**Separation of kalium jodatum crist. and morphinum hydrochloric. pulv.** HERMANN KUNZ-KRAUSE. *Pharm. Ztg.* 68, 185-6(1923).—In discussing this problem attention is directed to the possible incompatibility in compounding morphine-HCl with KI or KBr. W. O. E.

**The vermifuge "santoperonin."** BODINUS. *Pharm. Ztg.* 68, 186(1923); cf. *C. A.* 16, 2960; 17, 1529.—This prepn. contains traces of Na<sub>2</sub>SO<sub>4</sub> and about 38% CuO, an amt. far in excess of that claimed by the manuf. Treatment with dil. HCl or H<sub>2</sub>SO<sub>4</sub> effects instant sepn. of the prepn. into its org. and inorg. components, the former possessing apparently an azo grouping. The presence of salicylic acid was indicated by FeCl<sub>3</sub>. W. O. E.

**Cocaine adulterants.** P. BOHRISCH. *Pharm. Zentralhalle* 64, 107-9(1923).—Three cases are reported involving original packages of "E. Merck" with Na salicylate, naphthalene and B(OH)<sub>3</sub> as adulterants. Other forms of sophistication reveal the use

of  $\text{MgSO}_4$ , talc,  $\text{CaCO}_3$  and novocaine. Still another case involved the use of containers bearing label and seal of "Riedel." The contents showed no cocaine or other anesthetizing substance whatever, the bottles apparently having been first washed out with some mucilaginous material, partly dried and treated with crystals of  $\text{KClO}_3$ , then filled with a mixt. of  $\text{NaHCO}_3$ , and a siliceous substance contg. Ca, and  $\text{KClO}_3$ . W. O. E.

**The deterioration of drugs and how to prevent it.** J. W. ENGLAND. *Am. J. Pharm.* **95**, 71-80(1923).—A discussion of the properties of drugs, causes of deterioration and its prevention by the application of certain general principles, as illustrated by certain drugs. W. G. GAESSLER

**Bacterial preparations in common use.** LOUIS GERSHENFELD. *Am. J. Pharm.* **95**, 80-100(1923).—A lecture. W. G. GAESSLER

**Some notes on chloramine-T.** W. V. KOPFSTEIN. *Am. J. Pharm.* **95**, 101-4 (1923).—The prepn. of tablets of chloramine-T is discussed. The atm. should be free from acid and  $\text{NH}_3$  fumes and odors such as creosote, etc. The temp. for drying should not at any time be above  $100^\circ \text{F}$ ., since above this temp. decompn. is likely to set in. If the tablets have a tendency to turn yellow it is a sure indication that decompn. has started or will ultimately set in. W. G. GAESSLER

**Therapeutic novelties introduced in 1922.** S. RABOW. *Chem.-Ztg.* **47**, 129-30, 153-4, 158-9(1923). E. H.

**Tobacco cultivation for nicotine: *Nicotiana rustica* species.** J. DU P. OOSTHUIZEN. *J. Dept. Agr., Union S. Africa* **6**, 166-75(1923).—Varieties of *N. rustica* contain about 5% nicotine as compared to about 2% for varieties of *N. tabacum*. The growing of *N. rustica* for the prepn. of nicotine ext. appears to offer com. possibilities. The results of a large number of expts. carried out to det. the factors affecting the yield and nicotine content of *N. rustica* are summarized as follows: (1) Heavy applications of manure or other N fertilizers increase both the yield and nicotine content; (2) applications of lime on acid soils give marked increases in yields; (3) the best yields were obtained by setting the plants 12 in. apart in the row, but the nicotine content was not affected; (4) topping increases the nicotine content; (5) the nicotine content decreases if the plants are allowed to become over-ripe; (6) flue-curing gives a higher nicotine content than air-curing, but drying in the sun reduces the nicotine content considerably; (7) the nicotine content is lower when the whole plant is air-cured than when individual leaves are air-cured; (8) the nicotine content is higher when the tobacco is first green-sweated and then air-dried than when green-sweating is omitted. K. D. JACOB

**Determination of total geraniol content of citronella oil.** DE JONG AND A. RECLAIRE. *Perfumery Essent. Oil Record* **13**, 358(1922); cf. *C. A.* **17**, 180.—If the acetylated oil is accurately washed out and if pure  $\text{NaOAc}$  free from C and tarry matter is used for the acetylation the oil is not dark and the neutralization gives no trouble. As sapon. often darkens the oil, 50 cc. of water is added as a medium for the titration. The use of 20 cc. of 0.5 N KOH for the sapon. is an excess of 45% above the theoretical amt., and there is no object in using more. J. C. S. I.

**Allens's goiter treatment.** ANON. *J. Am. Med. Assoc.* **80**, 572-3(1923).—This prepn. is sold by the Allen Remedy Co. It is essentially a colored and flavored sirup, contg. 1.74 g. HI, 0.069 g.  $\text{NH}_4\text{I}$  and 0.83 g. of  $\text{FeI}_2$  per 100 cc. and 3.98% of  $\text{EtOH}$ . Extravagant therapeutic claims are made for it. L. E. WARREN

**Owl enamel cream.** ANON. *J. Am. Med. Assoc.* **80**, 1022(1923).—This is sold by the Owl Drug Co. in 2 colors, pink and white. Analysis of the pink variety was made because of severe poisoning in a patient who had used the prepn. for several years (Woltman, *J. Am. Med. Assoc.* **79**, 1685(1922)). When fresh the prepn. was a soft, pink, perfumed mass of about the consistency of putty. Analysis showed basic lead carbonate 42.5,  $\text{CaCO}_3$  40,  $\text{C}_2\text{H}_5(\text{OH})$  7, talc 0.5, Fe,  $\text{P}_2\text{O}_5$  and coloring traces and  $\text{H}_2\text{O}$

to make 100 %. No cautions concerning the dangerous nature of the prepn. are given.

L. E. WARREN

**The influence of hydrochloric acid in cinchona preparations.** W. L. SCOVILLE. *J. Am. Pharm. Assoc.* 12, 104-7(1923); cf. *C. A.* 16, 4014.—Red cinchona requires a larger proportion of acid for extn. and preservation than does the yellow. There is an optimum amt. for each variety. Less than the optimum amt. means less efficient extn. and more subsequent pptn. and a greater amt. of acid produces the same results. For yellow cinchona the best results are obtained by using about 1.5% of HCl based upon the wt. of the drug and employing the acid in the macerating menstruum. For red cinchona the most efficient proportion is 2.5 to 3% on the same basis. Recent observations on prepn. made in 1918-9 show that in neutral prepn.  $C_6H_5(OH)_3$  (10% in fl. exts. and 7.5% in tincts.) aids materially in preventing pptn. Sucrose and glucose are nearly as effective.  $C_6H_5(OH)_3$  should be added to percolate and not to the menstruum. Lactic acid is inferior to HCl in the extn. of the drug. Hot extn. is of no advantage over cold and may be a disadvantage through the formation of phlobaphenes.

L. E. W.

**The quantitative determination of sparteine in tablets.** P. W. JEWEL. *J. Am. Pharm. Assoc.* 12, 107-12(1923).—Sparteine is usually present in tablets as a salt. The tablets are dissolved in  $H_2O$  contg. a little acid and the alkaloid is removed and purified by the double shake-out method, with  $CHCl_3$  as the solvent. The solvent in the final shake-out is evapd. on the steam bath, with a current of air and a little  $Et_2O$  at the end. The container is removed as soon as the last portion of solvent has disappeared, the residue cooled and weighed. The alkaloid is slightly volatile at  $100^\circ$ , the loss being 3.19% after heating for 1 hr. and 6.6% after 7 hrs. The U. S. P. and the Jorissou tests are preferable to the Grant test for identification. Sparteine- $H_2SO_4$  may be titrated with 0.02 N NaOH with Me red or phenolphthalein as indicator; the latter is preferable. The picric acid method is unsatisfactory for quant. purposes because of the soly. of the salt in  $H_2O$ . It was found impossible to titrate the sepd. alkaloids after extn. by  $CHCl_3$  because of the uncertain end point. This is probably due to the brown color of the alkaloid and to oxidation. Shaking the alkaloid out from an  $Et_2O$  soln. with N acid and back titration was found impracticable.

L. E. WARREN

**A brief review of the crude drugs entered at the port of New York during the past year.** L. J. SCHWARZ. *J. Am. Pharm. Assoc.* 12, 200-41(1923).—Of 3500 shipments 210 were detained for one cause or another. Of the detained ones some were spurious, others were low in active principle and some yielded an excess of ash (generally due to dirt). On the whole the conditions of the drug shipments are not bad. L. E. W.

GILDEMEISTER, E. AND HOFFMAN, FR.: **The Volatile Oils.** Vol. III. 2nd Ed. by E. Gildemeister. Translated by Edward Kremers. New York: John Wiley & Sons. Reviewed in *Am. Perfumer* 18, 35(1923); cf. *C. A.* 14, 2053.

REUTTER, L.: **Treatise on Materia Medica and Vegetable Chemistry.** Paris VI.: J. Baillière & Son, 19 Rue Hautefeuille. 8 parts of 112 pp. F. 12 each plus 10% for mailing. Parts I, II & III now on sale. Reviewed in *Am. J. Pharm.* 95, 186(1923).

WOLFFENSTEIN, RICHARD: **Die Pflanzenalkaloide.** 3rd Ed. Berlin: Julius Springer. 506 pp. \$4.

**1,4-Arsenobenzaldehyde and similar compounds.** A. ALBERT. U. S. reissue 15,557, Mar. 6. See original pat. 1,425,931; *C. A.* 16, 4301.

**Synthetic drugs.** F. HOFMANN LA ROCHE AKT.-GES. Brit. 188,521, Nov. 1, 1921. A double compd. or quasi compd. of *C,C*-isopropylallylbarbituric acid and 1-phenyl-2,3-dimethyl-4-dimethylamino-5-pyrazolone is obtained by melting the two



components together in more or less equi-mol. proportions. The product has strong analgesic properties.

**Pancreatic preparations.** LEPDOGA SOC. ANON. Brit. 188,660, Nov. 7, 1922. A prepn. contg. the whole pancreas gland in a dry form is obtained by grinding the fresh or salt-pickled gland with anhyd. salts. *E. g.*, ground pancreas gland, plaster of Paris, well dried common salt, anhyd.  $\text{Na}_2\text{SO}_4$  and  $\text{NH}_4\text{Cl}$  are mixed to form a uniform, almost dry mass, which is then dried at low temp. and passed through a disintegrator. Cement may be partially substituted for plaster of Paris, anhyd.  $\text{MgSO}_4$  or anhyd. Na phosphate for the  $\text{Na}_2\text{SO}_4$  and  $\text{NH}_4(\text{SO}_4)_2$  or nitrate for the chloride. The prepn. is stated to have higher proteolytic and diastatic power than an equal wt. of dry product obtained by impregnating sawdust with the juice of the pancreas gland.

**Oxidized protalbinic and lysalbinic acids; medicinal preparations.** M. E. WOLVERKAMP. Brit. 188,772, Aug. 16, 1921. The alkali salts of oxidized protalbinic and lysalbinic acid, which are protective colloids for obtaining colloidal solns. of  $\text{HgO}$ ,  $\text{HgS}$  or Hg salicylate for medicinal purposes, are prepd. by oxidizing the alkali salts of protalbinic acid with  $\text{HgO}$ . It is not necessary to remove the Hg present in the product in view of the use for which it is intended. *E. g.*, serum albumin is heated with NaOH soln., filtered, and heated with  $\text{HgO}$  and additional NaOH at  $100^\circ$  after which glucose is added and the heating continued; the liquid is then decanted from Hg and pptd. with HCl, the ppt. being dissolved in the min. quantity of 2 *N* NaOH soln.; on evap. to dryness a mixt. of the Na salts of the two oxidized acids is obtained. The Na salts of the oxidized acids are obtained separately by a similar process starting from alk. soln. of protalbinic and lysalbinic acids, resp., but without the treatment with glucose.

**Extraction of alkaloids.** A. STOLL. U. S. 1,447,400, Mar. 6. Acid reagents are added to plant drugs to render the alkaloidal content of the drugs insol. in solvents of fatty substances of low b. p., *e. g.*, alc. and  $\text{C}_6\text{H}_6$ , and a solvent of this character is then used for removing impurities from the drug. After this preliminary treatment, the drug is suspended in a solvent of the same character and the mixt. is rendered alk. to cause the extrn. of the alkaloids by the solvent. The liberated alkaloid soln. is concd. and the alkaloids are purified by conversion into their salts and crystn. Treatment of belladonna leaves, pilocarpus leaves, aconite root, bark of *Corynanthe yohimbe* and opium are described.

## 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

**Sulfuric acid from gypsum.** W. DOMINIK. *Przemysl Chem.* 5, 185-91(1921).—Gypsum may be converted into  $(\text{NH}_4)_2\text{SO}_4$  and the latter into  $\text{NaHSO}_4$ , from which free  $\text{H}_2\text{SO}_4$  may be obtained by (1) reduction of the free acid to  $\text{SO}_2$  and re-oxidation, (2) distn. with ballast (cf. Moscicki and Dominik, *C. A.* 15, 2155), (3) crystn. of hydrated  $\text{Na}_2\text{SO}_4$  by cooling and concn. of the mother liquor.  $\text{Na}_2\text{SO}_4$  increases in soly. with addn. of free  $\text{H}_2\text{SO}_4$  to a max. above which the acid sulfate seps. The soly. also decreases rapidly with the temp.; at  $-11^\circ$  the max. soly. corresponding to 32% free acid is only about 4%  $\text{Na}_2\text{SO}_4$  by weight, so that at this temp. a fairly complete sepn. can be obtained in one operation. \*A calcn. of the water required and fuel consumption necessary for the decompn. of the acid salt at a given temp. is added. J. S. C. I.

**Causticization of soda ash.** J. HARROP AND H. O. FORREEST. *Ind. Eng. Chem.* 15, 362-3(1923).—The effect on the time of settling and the conversion, of the kind of lime, its ratio to the  $\text{Na}_2\text{CO}_3$  and the time of treatment are studied. F. C. Z.

**Reduction of calcium sulfate and magnesium sulfate by carbon monoxide, carbon and hydrogen sulfide.** J. ZAWADZKI, K. KOSSAK, AND H. NARBUT. *Przemysl Chem.* 5,

225-36(1921).—At temps. below 900°,  $\text{CaSO}_4$  is reduced to Ca sulfide; the reaction is quant. about 900°; the velocity of reaction is sufficient for technical purposes. The Ca sulfide yields  $\text{H}_2\text{S}$  quantitatively on heating with  $\text{MgCl}_2$  soln. Above 900°  $\text{CaO}$  and  $\text{SO}_2$  are also produced in quantities increasing with rise of temp.  $\text{MgSO}_4$  on reduction with CO is almost completely converted into  $\text{MgO}$ ,  $\text{SO}_2$ , and free S.  $\text{MgSO}_4$  reduced with  $\text{H}_2\text{S}$  above 700° yields  $\text{MgO}$  while  $\text{CaSO}_4$  under similar conditions is converted into Ca sulfide. The products of the reduction of  $\text{CaSO}_4$  and  $\text{MgSO}_4$  by C are dependent on the temp. and the ratio of C to sulfate; at lower temps. and with excess of C,  $\text{MgSO}_4$  leaves a residue contg.  $\text{MgS}$  as well as  $\text{MgO}$ ; in the case of  $\text{CaSO}_4$  the residue is sulfide only. At higher temps. and with less C the products are  $\text{MgO}$ ,  $\text{SO}_2$ , and S, and  $\text{CaO}$  and  $\text{SO}_2$ , resp. J. S. C. I.

**Evaporator design.** Influence of the properties of aluminium sulfate solutions. W. L. BADGER AND J. S. FRANCE. *Ind. Eng. Chem.* 15, 364(1923).—Approx. figures are given for the change in total solid content, f. p. and b. p. of commercial  $\text{Al}_2(\text{SO}_4)_3$  solns. with change in density from 35 to 65° Bé. W. L. BADGER

**Adulteration of potassium iodide with potassium bromide.** J. GROSSMANN. *Pharm. Ztg.* 67, 689(1922); *J. Soc. Chem. Ind.* 41, 706A(1922).—Attention is directed to the adulteration of KI with KBr (25% or more), and to the inadequacy of the usual test for bromide (sparing soly. of  $\text{AgBr}$  in  $\text{NH}_3$ ). Particular attention should be given to the behavior of the  $\text{AgI}$  ppt., which in the presence of  $\text{AgBr}$  darkens more rapidly on exposure to light. In doubtful cases the ppt. should be tested for bromide by distn. with  $\text{FeCl}_3$ . W. O. E.

**The world's potassium requirements and sources.** BIRGER CARLSON. *Stenskt Kem. Tids.* 35, 34-60(1923).—The potassium economics problem is discussed in its broader aspects. Analytical and statistical information are given. A. R. ROSE

**Researches on natural and artificial graphite.** K. ARNDT AND F. KÖRNER. *Z. angew. Chem.* 35, 440-3(1922).—The sp. resistance of rods pressed from different varieties of natural and artificial graphite has been detd. The results show that the sp. elec. resistance of graphite depends principally on the grain size and ash content, while the shape of the grains has also a slight influence. The resistance increases with increasing ash content and decreases with increasing size of the grains. In the case of graphitized electrodes the resistance depends chiefly on the vol. of the pores and on the actual graphite content, a decrease in the former and an increase in the latter reducing the resistance. A curve has been constructed for the sp. resistance of mixts. of graphitized and ungraphitized gas C compressed into rods, from which, by observing the resistance of a graphitized anode of unknown compn., a rough idea of the amt. of contained graphite may be obtained. The resistance of a no. of mixts. of graphite and powd.  $\text{MnO}_2$ , such as are used in battery anodes, is represented graphically; the addn. of the  $\text{MnO}_2$  very slightly increases the resistance up to a content of 50-60%, after which an exceedingly rapid increase is observed. J. S. C. I.

**Physical properties of dental cements.** II. PAUL PORTSCHKE. *Ind. Eng. Chem.* 15, 339-42(1923); cf. *C. A.* 10, 1226.—Methods and app. are described for detg. the heat generation, texture, permeability and setting time of Zn oxyphosphate cements. The heat generated in setting varies considerably in different brands. The heat can be varied greatly by the rate of addn. of powder to liquid and the time of mixing. By proper mixing no brand should cause damage. Crushing strength is directly proportional to heat generation, cements evolving the most heat having the highest crushing strength as well as the finest texture. The texture varies from fine vitreous to coarse chalky. The latter texture is the more permeable to aq. fluids. Cements of fine vitreous texture are impermeable to dye solns. Com. designations for hardness such as "slow," "rapid," etc., are of slight significance, for there is recognized no standard time of set. A cement

setting at room temp. relatively faster than another may be relatively slower at body temp. Those showing the greatest strength, the finest texture, the least permeability and the greatest heat liberation on setting show the greatest increase in strength between the 15-min. and 24-hr. period of setting. The ideal cement should set slowly at room temp. and rapidly at body temp.

C. C. DAVIS

Atmolysis of the gaseous mixture used in the manufacture of sulfuric acid by the contact process (URBAIN, URBAIN) 2. Potash possibilities in Illinois (SCHROYER) 8.

KLEHE, THEODOR: *Der Kalk*. Berlin: Selbstverlag. d. Vereins deutscher. Kalkwerke. 20 pp. M 4.50.

Nitric acid by means of the electric arc. W. SIEBERT. Can. 228,883, Feb. 20, 1923.—A N-O mixt. is treated in an elec. arc, the resulting gases are cooled, the  $\text{HNO}_3$  formed is absorbed and the unabsorbed gases are returned for further treatment whereby they are mixed with pure O and N to maintain a gas mixt. contg. 50% N and 50% O. App. is also specified. Cf. C. A. 17, 693.

Arsenic and hydrochloric acids. C. ELLIS and V. T. STEWART. U. S. 1,447,937, Mar. 6. A stream of a suspension of at least 11% of  $\text{As}_2\text{O}_3$  in  $\text{H}_2\text{O}$  is caused to flow in contact with a gas contg. free Cl to form HCl and  $\text{H}_3\text{AsO}_4$ .

Calcium arsenate. C. ELLIS and V. T. STEWART. U. S. 1,447,938, Mar. 6. A concd. aq. soln. of  $\text{H}_3\text{AsO}_4$  is added to an excess of pulverized quicklime with agitation and the addn. is regulated so as to maintain the materials in a non-pasty pulverulent condition during the reaction.

Tricalcium arsenate. C. ELLIS and V. T. STEWART. U. S. 1,447,203, Mar. 6.  $\text{As}_2\text{O}_3$  is oxidized with Cl, while hot, and subsequently in cold aq. soln., and the arsenic acid formed is reacted on with  $\text{Ca}(\text{OH})_2$  to form tri-Ca arsenate.

Ammonia synthesis. NITROGEN CORPORATION. Brit. 188,651, Oct. 31, 1922. To facilitate the insertion and removal of the catalytic material, an autoclave for the synthesis of  $\text{NH}_3$  is provided at both the upper and lower ends with a special closure capable of withstanding high temps. and pressures.

Catalytic ammonia production. L. CASALE. U. S. 1,447,123, Feb. 27. See Can. 225,824 (C. A. 17, 857).

Ammonium sulfate. G. ROYSTON. Brit. 188,587, Jan. 10, 1922. In app. for the neutralization of  $(\text{NH}_4)_2\text{SO}_4$  in its wet state as received direct from the saturator, the salt is circulated through the app. with  $\text{NH}_3$  gas and steam until the neutralization has been effected. A suitable app. is specified.

Basic calcium hypochlorites. CHEMISCHE FABRIK GRIESHEIM-ELEKTRO. Brit. 188,662, Nov. 8, 1922. Addn. to 182,927 (C. A. 16, 4303). In the process of the principal patent for the production of basic Ca hypochlorites by the chlorination of  $\text{Ca}(\text{OH})_2$  in  $\text{H}_2\text{O}$ , the chlorination is so controlled that individual basic hypochlorites or mixts. of these in definite proportions are produced. The chlorination is allowed to proceed, with pptn. of basic hypochlorite, until the concn. of bleaching Cl in the mother liquor has attained a min. value and begun to increase, when it is found that the ppt. consists of the dibasic hypochlorite. On further chlorination the % of bleaching Cl in the mother liquor continues to increase, and then falls to another min. value, at which point the solid ppt. present consists almost entirely of the monobasic compd. By terminating the chlorination at corresponding points where the concn. of bleaching Cl in the mother liquor decreases, mixts. of these two compds. or of the monobasic compd. with neutral hypochlorite may be obtained.

Sulfates. J. S. WETZLAR. Brit. 188,868, Sept. 30, 1921. Metals or alloys not

readily sol. in  $\text{H}_2\text{SO}_4$  are converted into sulfates by first dissolving in  $\text{HNO}_3$ , and then adding  $\text{H}_2\text{SO}_4$  to convert the nitrates into sulfates. During both stages air is blown into the soln. to remove the N oxides and  $\text{HNO}_3$ , and  $\text{HNO}_3$  is recovered of sufficient strength for subsequent use. The sulfate is sepd. by crystn. and the mother liquor which contains  $\text{HNO}_3$  may be used again. The process may be used for the treatment of Cu, Ni and brass. The production of Cu Mg sulfate is also mentioned.

**Treating silicates.** PLAUSON'S (PARENT Co.), LTD. Brit. 188,454, Sept. 16, 1921. Insol. minerals contg. alkali metals, such as feldspar, are heated with fusible salts at a temp. not higher than about  $650^\circ$  or less if the heating is effected under pressure. The reaction mixt. is extd. with  $\text{H}_2\text{O}$  and the sol. alkali salts are sepd. in the known manner. Suitable fusible salts are: the chlorides of Ca, Ba, Fe, Zn, Mn, and Al;  $\text{MgSO}_4$ ; and  $\text{NaNO}_3$ . Mixts. of these salts may be employed.

**Sodium phosphate.** W. GLAESER. U. S. 1,447,544, Mar. 6. Na phosphate is formed by treating phosphate rock with a soln. contg. niter cake and NaCl, heated to about  $500^\circ$ .

**Sodium sulfide.** F. G. STANTIAL and J. H. CLARKE. U. S. 1,447,524, Mar. 6. Na sulfate in the form of a molten non-flowing film is reduced with granular petroleum coke to form sulfide. The coke granules become coated with Na sulfate and are then heated to about  $800^\circ$  or higher.

**Sodium nitrate.** GUGGENHEIM BROS. Brit. 188,634, July 5, 1922. In the extn. of  $\text{NaNO}_3$  from caliche, the reduction of yield consequent on the formation of the double salt  $\text{NaNO}_3\text{-Na}_2\text{SO}_4$  is avoided by adding reagents having a greater affinity for  $\text{Na}_2\text{SO}_4$  than has  $\text{NaNO}_3$ . The reagents mentioned are K, Mg, and Ca compds., particularly  $\text{MgSO}_4$ ,  $\text{CaSO}_4$ , syngenite (Ca K sulfate) and astrakanite (Mg Na sulfate). Sometimes caliche contains glauberite or other impurities having similar effect, and in that case caliches not contg. such compds. may be mixed with a caliche contg. such compds. In any case, the leaching is so conducted that these advantageous compds., whether originally present or added, are not removed during the process. One effect is that the  $\text{Na}_2\text{SO}_4$  remains behind with the slimes, rendering the slimes readily filterable. The leaching is effected at temps. from atm. to  $58^\circ$  and the cooling to sep. the nitrate is carried to  $7^\circ$  or such lower temp., occasioned by the impurities present, as may be possible without causing crystn. of  $\text{Na}_2\text{SO}_4$ . Substances which allow of such lower temps. are particularly K and Mg salts, iodates and borates.

**Chrome alum; chromium salts.** KINZLBERGER & Co. Brit. 188,338, Nov. 3, 1922. Cr compds. free from Fe are prepd. by dissolving Fe-Cr in  $\text{H}_2\text{SO}_4$ , adding  $\text{CaCO}_3$  or its equiv. in quantity insufficient to ppt. all the Cr, dissolving out the Cr from the ppt. by an acid, such as  $\text{H}_2\text{SO}_4$ , and, when chrome alum is desired, adding  $\text{K}_2\text{SO}_4$  to obtain the alum. The filtrate is treated with another quantity of  $\text{CaCO}_3$ , etc., to ppt. the rest of the Cr together with some Fe and the ppt. is treated with  $\text{H}_2\text{SO}_4$  to dissolve the Cr and Fe. The soln. is then mixed with  $\text{H}_2\text{SO}_4$  to be used in dissolving more Fe-Cr.

**Treating copper-bearing substances.** C. S. BRADLEY. Can. 228,780, Feb. 20, 1923. Cu-bearing materials are treated with a  $\text{CaCl}_2$  soln. to dissolve the Cu which is then pptd. as trioxychloride by the addn. of  $\text{CaCO}_3$ , which also regenerates the  $\text{CaCl}_2$  for reuse.

\* **Apparatus for purification of brine for washing sodium chloride.** SAKI HOSHINO. Japan. 40,209, Oct. 5, 1921. The app. is made by combining spraying, pptg., and dissolving vessels for NaCl and a mixing vessel for  $\text{BaCl}_2$ , etc. The waste brine (1801) used for the washing of crude NaCl is mixed with alum (about 4 g.) and sprayed for complete mixing.

**Titanium-nitrogen compounds.** F. VON BICHOWSKY and J. HARTMAN. Brit. 188,558, Dec. 7, 1921. Ti-N compds. are produced by heating a mixt. of ilmenite, C,

and an alkali-metal compd. contg. O but not contg. S, in the presence of N or gaseous mixts. contg. the same, the temp. being slightly below the m. p. of the mass. The C may be supplied as soot, coke, or a compd. contg. C, such as crude oil, and these materials may be supplemented, or even supplanted, by gaseous mixts. contg. hydrocarbons, such as natural gas. Examples are given. Cf. *C. A.* 16, 319, 1641.

**Lead monoxide.** T. GOLDSCHMIDT AKT.-GES. Brit. 189,132, Nov. 15, 1922. Metallic Pb, litharge or a suitable Pb compd. such as the carbonate or sulfide is volatilized and oxidized completely to monoxide. The PbO is sepd. by any suitable means such as filtration or washing.

**Apparatus for burning sulfur.** H. D. WELLS. Can. 228,631, Feb. 6, 1923.

**Sulfur combustion furnaces.** A. HANSEN. Can. 228,807, Feb. 20, 1923.

**Decolorizing carbon.** KIUCHI MIYAKE. Japan. 40,301, Oct. 13, 1921. Chemically pptd. silicic acid is powdered to pass a 70-mesh sieve. 2.4 kg. of the powder is homogeneously mixed with 57 kg. of heavy mineral oil and heated in a closed retort at 500° until there is no further evolution of volatile matter; then the retort is heated at 1,000° for 30 min. and the product is cooled and crushed. In addition to heavy mineral oil, pupa oil and other animal and vegetable oils, or tar or pitch derived from them, may be used. The distd. part is a cracked oil and permanent gases may be used as a fuel.

**Revivifying absorbents.** NAAMLOOZE VENNOOTSCHAP ALGEMEINE NORIT MAATSCHAPPIJ (known as General Norit Co., Ltd.). Brit. 188,672, Nov. 13, 1922. Addition to 104,456 (*C. A.* 11, 1893). An app. for revivifying finely divided decolorizing C, as described in the principal patent, is modified by forming the condensation and dust-collecting app. of a plurality of units, each connected to the heating cylinders by short and wide conduits to prevent choking by accumulation of dust and to facilitate cleaning.

**Decolorizing material containing carbon and colloidal substances.** L. WICKENDEN. U. S. 1,447,452, Mar. 6. Porous decolorizing C carrying colloidal material in its pores is prepd. by satg. C from wood pulp waste liquor with a 2% aq. colloidal soln. of  $\text{Al}(\text{OH})_3$  and drying.

**Decolorizing and filtering agent.** P. A. BOECK. Can. 228,861, Feb. 20, 1923. A decolorizing agent contains infusorial earth and fuller's earth in equal proportions by wt. The infusorial earth reduces the tendency to clogging and presents a larger surface of the fuller's earth.

**Reactivating spent catalyzers.** W. D. RICHARDSON. U. S. 1,447,689, Mar. 6. Finely divided catalyzers such as the residue of Ni catalyzers remaining after hydrogenation of oil are reactivated by treatment with H at 200–250° while admixed with a small amt. of oil.

**Phenol condensation product.** L. H. BAEKELAND and A. H. GOTTHELF. Can. 228,557 Feb. 6, 1923. Phenol is mixed with paraldehyde or AcH in the presence of strong HCl and water is added. The product formed on heating is insol. and infusible up to 218° and melts at a higher temp. The product may be treated with a hardening agent such as formaldehyde, paraformaldehyde or hexamethylenetetramine.

**Brake lining.** W. D. PARDOE. U. S. 1,447,100, Feb. 27. A folded fabric with diagonal ribs or twills is impregnated with frictional binding material, *e. g.*, a rubber compn.

**Impregnating clutch rings.** L. KIRSCHBRAUN. U. S. 1,447,347, Mar. 6. Rings cut from a stock contg. Cu wool or steel wool, asbestos and paper stock or other combustible fiber are satd. with a mixt. of gas oil and asphalt and then baked at a temp. sufficiently high to burn out the organic fiber and effect oxidation of the impregnating compn.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**Glass furnace temperatures.** LOESER. *Keram. Rundschau* 30, 48(1922).—In the flame of a Nchse-Dralle furnace of the basin system, a temp. of 1600–1650° was detd. On the surface of the glass the temp. was 1497–1526°. In the two flues, one was 1320°, the other 1385°.

O. P. R. OGILVIE

**The continuous system of grinding ceramic materials.** H. HARDINGE. *J. Am. Ceram. Soc.* 6, 548–62(1923).—Several grinding plants are well described and illustrated.

C. H. KERR

**The value of screen analysis in ceramics.** F. P. NICKERSON. *J. Am. Ceram. Soc.* 6, 563–78(1923).—The Tyler standard screen scale has openings in successive sizes which increase in the ratio of  $\sqrt{2}$  or 1.414. This gives a practical range of sizes and the logarithmic plotting of results is both convenient and advantageous.

C. H. KERR

**Preliminary report on the residual kaolin and feldspar in the Pacific Northwest.** H. WILSON, A. L. BENNETT AND P. T. HEATH. *J. Am. Ceram. Soc.* 6, 475–90(1923).—The residual cryst. kaolins of eastern Wash. and northwestern Idaho, when well selected and purified, compare favorably with English China clay. Com. quantities of feldspar, quartz and fireclay are also available. The weathering of the kaolin has been very complete and the resulting plasticity may permit the omission of the usual ball clay in the body. Some flux may be required, however, to give the proper vitrification.

C. H. KERR

**Diaspore clay of Arkansas and Missouri.** D. C. WYSOR. *J. Am. Ceram. Soc.* 6, 501–9(1923).—Arkansas diaspore exists only in certain bauxite oolites and probably constitutes not over 1% of the deposits. The rest of the hydrate composing the ore bodies is gibbsite. Diaspore is more stable than gibbsite. Bauxite may be an unstable dihydrate. The com. deposits of diaspore in Mo. are sedimentary. The diaspore is always surrounded by clay. The normal Mo. diaspore deposit will run:  $H_2O$  13.5,  $Al_2O_3$  65.0,  $SiO_2$  15.0,  $TiO_2$  4.0,  $Fe_2O_3$  1.2,  $CaO$  0.1,  $MgO$  0.2,  $KNaO$  1.0. It will fuse at cone 38–39. There is about 1 cone difference for each 4–5%  $Al_2O_3$ . The "burley" clay carries about 45–50 or possibly 55%  $Al_2O_3$ .

C. H. KERR

**Composition and properties of diaspore, bauxite and gibbsite.** R. M. HOWE AND R. F. FERGUSON. *J. Am. Ceram. Soc.* 6, 496–500(1923).—Bricks high in  $Al_2O_3$  may be made from diaspore (the monohydrate), gibbsite (the trihydrate) or bauxite (a mixture of the two). The ores vary widely in compn. The fusion points are lowered most by  $CaO$  and least by  $Fe_2O_3$  and  $SiO_2$ . Burning shrinkage was lowest in those minerals high in  $SiO_2$  and highest in those high in  $Fe_2O_3$ . Gibbsite showed a higher burning shrinkage than diaspore. The chief defect of high  $Al_2O_3$  bricks is excessive shrinkage.

C. H. KERR

**China clay. Its composition, preparation and uses.** H. F. COLLINS. *Chemistry & Industry* 42, 88–91, 114–7(1923).—A description of the compn., distribution, methods of working, purification, uses and economic importance of china clay.

C. C. D.

**The effect of heat treatment and composition of semi-porcelain bodies on crazing.** I. E. SPROAR. *J. Am. Ceram. Soc.* 6, 510–24(1923).—The thicker the glaze the greater its tendency to craze. Hand dipping is not uniform. There is need of a mechanical dipper. Biscuit burning should be uniform to insure uniform absorption. The glaze used was 0.027  $Na_2O$ , 0.202  $K_2O$ , 0.422  $CaO$ , 0.213  $PbO$ , 0.136  $ZnO$ , 0.256  $Al_2O_3$ , 0.240  $B_2O_3$ , 2.354  $SiO_2$ . Any changes to decrease crazing were at the expense of other desirable properties. Adding 10–20% of "Hercules" clay to the body greatly decreased the tendency to craze, but no other body change was found to be feasible. The greatest

resistance to crazing was at 7-12% absorption. Increased absorption does not always mean increased crazing. Increasing the time of firing at maturing temp. decreased the tendency to craze.

C. H. KERR

Studies of changes in the physical properties of a hard porcelain caused by varying the feldspar from sodium to potassium feldspar and by varying the burning treatment. E. RORH. *Spektsaal* 55, 533-4(1923).—Porcelains of the following general compn. were studied: clay 50, quartz 25 and feldspar 25. K and Na feldspars of the following respective compns. were used:  $\text{SiO}_2$  64.3, 67.1;  $\text{Al}_2\text{O}_3$  19.4, 20.3;  $\text{Fe}_2\text{O}_3$  0.1, 0.3;  $\text{CaO}$  tr., 0.8;  $\text{MgO}$  0.4, tr.;  $\text{K}_2\text{O}$  12.9, tr.;  $\text{Na}_2\text{O}$  2.1, 11.8; ignit. loss 0.6, 0.1%. Mixts. varied from pure Na feldspar to pure K feldspar. Porcelains were fired to cones 9, 11-12, 13, 14, 15, 15-16. A study of thin section showed that at  $1120^\circ$  the feldspar melted. Upon increasing the temp. a portion of the clay substance went into soln. and the sillimanite crystallized out. The coarse grains of cryst. quartz did not go into soln. until a temp. of  $1480$ - $1500^\circ$  was reached. Upon further heating the sillimanite crystals were taken into soln. until at  $1600^\circ$  a homogeneous body was obtained. Conclusions: (1) The K porcelains produce bodies having a higher viscosity than the Na porcelains. (2) The K feldspars dissolved 20% clay and the Na feldspar dissolved 15% clay. (3) The soly. of  $\text{SiO}_2$  in the glass depends upon the size of grain, cryst. modification and firing temp. (4) Na feldspar exerts a stronger solvent action upon  $\text{SiO}_2$  than K feldspar. (5) Max. shrinkage occurred at cone 9 and above this the mass commenced to swell. (6) The sp. grs. of both the Na and K bodies decreased with an increase in firing temp. (7) The linear coeff. of expansion decreased up to cones 11-14. (8) The translucency increased up to cones 12-14, remained about the same between cones 12 and 14 and increased again above cone 14 when the coarse quartz grains were dissolved. The Na bodies were slightly more translucent than the K bodies. (9) The impact cross-breaking test and the ball compression test gave a max. at the temp. where max. shrinkage and d. were developed. (10) Both the K feldspar and the Na feldspar bodies gave a dielec. const. of 5.8. The elec. penetration depends largely upon the porosity of the body.

H. G. SCHURECHT

Deformation studies of silicates and aluminium silicates of the alkalies. B. A. RICER. *J. Am. Ceram. Soc.* 6, 525-47(1923).—The 2 ternary systems  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  and  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  were studied. In each system 2 areas of low fusibility were found, one with high alkali, low  $\text{SiO}_2$  and low  $\text{Al}_2\text{O}_3$  and the other with high  $\text{SiO}_2$ , low alkali and low  $\text{Al}_2\text{O}_3$ . In both systems the high  $\text{SiO}_2$  area was studied chiefly, because of practical ceramic value. In each system 3 eutectics (2 binary and 1 ternary) were found: 1.00  $\text{K}_2\text{O}$ , 1.291  $\text{SiO}_2$ ,  $780^\circ$ ; 1.00  $\text{K}_2\text{O}$ , 7.43  $\text{SiO}_2$ ,  $880^\circ$ ; 1.00  $\text{K}_2\text{O}$ , 0.276  $\text{Al}_2\text{O}_3$ , 6.978  $\text{SiO}_2$ ,  $870^\circ$ ; 1.00  $\text{Na}_2\text{O}$ , 0.972  $\text{SiO}_2$ ,  $830^\circ$ ; 1.00  $\text{Na}_2\text{O}$ , 4.579  $\text{SiO}_2$ ,  $860^\circ$ ; 1.00  $\text{Na}_2\text{O}$ , 0.185  $\text{Al}_2\text{O}_3$ , 4.55  $\text{SiO}_2$ ,  $800^\circ$ . Pound for pound  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  have the same fluxing value, when introduced in the form of carbonates.

C. H. KERR

\* Coloration, discoloration and other burning effects. ELLIS LOVEJOY. *Clayworker* 79, 38-9(1923).—Many discolorations are due to S gases and condensation of moisture on the ware in colder parts of the kiln. Remedies lie in slower water smoking, better circulation, more open kiln bottoms and stronger draft.

J. W. HEPPLEWHITE

The effect of uranium oxide upon the fusibility of Zettlitz kaolin. O. KALLAUNER AND J. HRUDA. *Spektsaal* 55, 523(1923).—In order to det. the effect of  $\text{U}_3\text{O}_8$  upon Zettlitz kaolin mixts. of varying compns. were melted in an electric furnace. The kaolin had the following analysis:  $\text{SiO}_2$  47.39,  $\text{Al}_2\text{O}_3$  37.74,  $\text{Fe}_2\text{O}_3$  +  $\text{TiO}_2$  0.72,  $\text{CaO}$  0.16,  $\text{K}_2\text{O}$  0.52, ignit. loss 13.58%. The softening points for various amts. of  $\text{U}_3\text{O}_8$  were 0, cone 35; 1%, cone 34; 5, 33; 10, 32; 20, 31; 40, 18; 50, 15; 60, 17; 80, 30; 90, 34-5; 100, 35+.

H. G. SCHURECHT

Antimony yellow glazes. W. ROHN. *Keram. Rundschau* 31, 31(1923).—A study was

made of antimony yellow, Pb glazes at cone 3a. Success depends upon (1) the constituents of the glaze, (2) an oxidizing kiln atm., and (3) a certain transparency of the glaze. Excellent results were obtained with glazes having an RO composed of 0.8 to 0.9 PbO and 0.1 to 0.2 KNaO. Good colors were also obtained with glazes having an RO composed entirely of PbO. Extra good colors were obtained with glazes having 0.1 to 0.2 Na<sub>2</sub>O and 0.8 to 0.9 PbO. This produced Neapolitan yellow shades. The alk. earths, with the exception of MgO, destroy the yellow color. Although MgO prevents to a certain extent the formation of the desirable Neapolitan yellow shades it does not destroy the yellow color as CaO does. BaO acts very similarly to CaO while a glaze contg. 0.8 PbO and 0.2 SrO<sub>2</sub> produces a white glaze entirely destroying the yellow color. ZnO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> do not have much influence on the yellow color. B<sub>2</sub>O<sub>3</sub> does not affect the color but gives the glaze a high gloss. The addn. of a small % Fe<sub>2</sub>O<sub>3</sub> to a yellow glaze produces an orange yellow. Opalescent yellow glazes have a dirty color; they are similar to China reds in this respect. 1 to 3% HSb<sub>2</sub>O<sub>3</sub> gives the best colors. The addn. of 6% SnO<sub>2</sub> to a yellow glaze changes its color to ochre. By changing the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> contents, glazes suitable for stoneware may be prepd. These glazes may also be used for china painting. By varying the PbO and Sb<sub>2</sub>O<sub>3</sub> contents a series of colors varying from S-yellows to orange-yellows can be prepd. Nine formulas for yellow glazes are given.

H. G. SCHURECHT

**Dry pressing refractory shapes.** L. W. FLOOD. *Brick Clay Record* 61, 865-6 (1922).—A high % of plastic clay is not essential for dry-press ware. Moisture content of dry-press ware usually runs about 7%. The advantages claimed in making large shapes by the dry-press process are: (1) Cost of manuf. is reduced. (2) Cost of installing expensive dryers or dry floors is lessened. (3) The ware is more uniform and exact in size. (4) Refractoriness of some clays is increased. (5) Uniform size of ware reduces the fireclay used in the joints. (6) Large refractory shapes withstand thermal shock much better. (7) Dry-press ware is a poorer conductor of heat. J. W. HEPPLEWHITE

An automatic direct-reading laboratory scale for weighing briquets (SCHURECHT) 1. Rotary inclined horizontal drying drums [for loam and clay] (U. S. pat. 1,447,929) 1.

BLACK, J. H.: **Manual of Face Brick Construction.** Milwaukee, Wis.: C. N. Caspar. 116 pp. \$9.

SEARLE, ALFRED B.: **Manufacture and Uses of Abrasive Materials.** London: Pitman. 127 pp. 2s. 6d.

STARK, JOHANNES: **Die physikalisch-technische Untersuchung keramischer Kaoline.** Leipzig: J. A. Barth. 145 pp. M 160.

**Glass.** GENERAL ELECTRIC CO. Brit. 188,451, Sept. 14, 1921. Transparent SiO<sub>2</sub> glass is made by fusing SiO<sub>2</sub> in a vacuum and then compressing the fused mass while plastic to reduce enclosed bubbles. A suitable construction is specified.

**Glass.** CORNING GLASS WORKS. Brit. 189,126, Nov. 14, 1922. A part of an app. for molding glass is made from steel contg. Cr 10-15 and Co 0.5-5%. Another suitable steel contains approx. Cr 13, Mn 0.5, Co 0.6, and C 0.35%. Another steel contains Cr and about 4% of Si. Molds made from these steels have a longer life than molds made from cast Fe, and they are particularly suitable for use with a glass that requires to be worked at a high temp.

**Glass.** TOSAKU YOSHIOKA. Japan. 40,242, Oct. 6, 1921. When superheated steam is passed into a mixt. of silicates and NaCl heated below its m. p., the reaction 2NaCl + SiO<sub>2</sub> + H<sub>2</sub>O = Na<sub>2</sub>SiO<sub>3</sub> + 2HCl takes place. The silicate is then melted with suitable materials for glass. E. g., a mixt. of SiO<sub>2</sub> 100, CaO 22 and NaCl 33 is heated at



about 700° in a rotating furnace, into which superheated steam is then passed; a porous mass of silicate is smoothly produced.

Glass. E. C. SULLIVAN and W. C. TAYLOR. Can. 228,865, Feb. 20, 1923. A glass has a combined silica and alkali percentage compn. over 90 and a mol. ratio of alkali to silica between 26 and 29 to 100 and a mol. ratio of bivalent oxides to silica between 7 and 10 to 100. Cf. C. A. 16, 2973.

Glass. W. C. TAYLOR. Can. 228,866, Feb. 20, 1923. A glass with a low sp. gr. contains at least 3% B<sub>2</sub>O<sub>3</sub> and a sulfate salt. Cf. C. A. 17, 1313.

Apparatus for bending continuous-sheet glass. J. P. CROWLEY and C. A. ROWLEY. U. S. 1,447,647, Mar. 6.

Leer conveyer for continuous-sheet glass. F. E. DEULIN. U. S. 1,447,648, Mar. 6.

Leer conveyer for continuous-sheet glass. H. S. DRUPY. U. S. 1,447,649, Mar. 6.

Apparatus and method for drawing two sheets of glass in separable contact with each other. A. E. FOWLE. U. S. 1,447,654, Mar. 6.

Apparatus and method for flattening sheet glass. S. B. HENSHAW. U. S. 1,447,661, Mar. 6.

Drawing sheet glass. J. WHITTEMORE. U. S. 1,447,702, Mar. 6. Mech. features:

Muffle leer furnace adapted for annealing glass. C. L. SHARP. U. S. 1,447,633, Mar. 6.

Coating ceramic ware. METALLISATOR GES. Brit. 189,085, May 24, 1922. Ceramic cooking vessels are coated with Al or Fe. The vessels are heated to a temp. of 300–400° and the metal is applied by any of the known metal dusting processes.

Enameling oven. D. LEISSLER. U. S. 1,447,795, Mar. 6. The oven is adapted for baking glazed articles.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

Thermochemical research on cement. R. NACKEN. *Zement* 11, 245–7, 257–8 (1922).—N. deals with the drying of cement in rotary driers at about 500°, the expulsion of CO<sub>2</sub> at 900°, incomplete burning between 1000° and 1250°, in which stage exothermic reactions occur, burning at 1250°, and finally strongly burning at 1400° or higher. The development of heat in the burning of cement is slow below the stage at which CO<sub>2</sub> is expelled. The heat of reaction begins to increase slowly at 930° and rises from 120 to 500 cal. per g., then more slowly to 600 cal. per g. The max. is at about 950°. As soon as the CO<sub>2</sub> is expelled, a vigorous reaction occurs, i. e., the formation of Ca silicates and aluminates, this reaching a max. at 960°, after which equil. is very quickly reached. Different results obtained in tech. practice are due to heterogeneity of the raw materials and the fact that some Ca carbonate has escaped burning until the end. It is calcd. that the quantity of heat required to burn 1 kg. of clinker up to a temp. of 1400° is about 900 cal.

J. S. C. I.

Improvements in the manufacture of magnesia cement. B. HAAS. *Chem.-Ztg.* 46, 88–9 (1922).—Crude MgCl<sub>2</sub> liquors contg. KCl, NaCl, and MgSO<sub>4</sub> so often used in making MgO-MgCl<sub>2</sub> cement make a product which dries more slowly, has less hardness, discolours more easily and requires more mechanical treatment but shows less blowing and sweating than one made from a pure MgCl<sub>2</sub> soln. of the same concn. Because of such properties and the greater cost of transport of liquor, the relative economy of the 2 methods must be calcd. for each case. Pure MgCl<sub>2</sub> solns. for a given purpose should be made 2–3° Bé. less concd. than the proper crude liquor. MgSO<sub>4</sub> is of advantage in preventing discoloration and blowing, particularly if weathering occurs under warm and dry conditions. • Because of its cost, MgSO<sub>4</sub> can be replaced by by-product kieserite. This has

proved so efficient that all  $MgCl_2$  has been replaced by kieserite and the product is non-hygroscopic and free from blowing, though the rate of drying and hardening is slower and the strength and toughness are less. By replacing  $MgCl_2$  by 15% more than its equiv. wt. of kieserite, a product is obtained with satisfactory tenacity. Replacement of part of the  $MgCl_2$  by metallic salts, particularly Fe salts, gives a product with less blowing and sweating and with toughness, color and good hardening qualities. Fe salts can also be used advantageously with  $MgSO_4$  or with kieserite to obtain pleasing colors.

C. C. DAVIS

The injurious effect of even the smallest contamination of cement and of concrete by sugar. F. HUNDESHAGEN. *Z. angew. Chem.* 36, 53-4(1923).—The failure of new concrete in a sugar warehouse to set was attributed after analysis to the presence of traces of sugar. The particular concrete which did not harden contained 0.06-0.08% sugar, whereas in a portion of the structure of the same concrete which did set, no sugar could be detected. Exptl. tests of mixts. of gravel, sand and cement contg. varying amts. of sugar were then made. Cement with 0.1% sugar, corresponding to approx. 0.02% of the dry concrete, set very slowly and its hardness was considerably reduced. With 1% sugar (0.2% in dry concrete) hardening was extremely slow and incomplete and the product was weak and friable. Addn. of 5% sugar (1% in dry concrete) was less injurious. The rate of hardening was almost normal, but after some time a whitish efflorescence appeared on the surface. Superficially the concrete appeared of normal hardness, but the interior was friable with many fissures. All samples contg. sugar gave a dull hollow sound when struck with a hammer. Approved grades of portland cement were mixed (1) with 30% by wt. of  $H_2O$  and 0.0, 0.1, 1.0 and 5.0% of sugar and (2) with 30% by wt. of 0.0, 0.1, 1.0 and 5% sugar solns. and let stand 14 days on glass. Those contg. no sugar were hard enough in 24 hrs. to give a ringing noise when struck. Those with 0.1% sugar remained for days weak and friable and gave a dull, hollow noise when struck. With 1.0% sugar the samples were very weak and fragile, could not be removed from the glass after drying without crumbling and shattered when struck. The samples with 5% sugar were fairly hard after 1-2 days, with a whitish efflorescence on the surface. In time the surface developed a network of cracks through shrinkage.

C. C. DAVIS

The determination of an equilibrium between cement and lime water. RICHARD LORENZ AND GUSTAV HÄGERMANN. *Z. anorg. allgem. Chem.* 113, 193-201(1921).—A cement analyzing in %  $SiO_2$  19.94,  $CaO$  64.38,  $Al_2O_3$  6.45,  $Fe_2O_3$  2.92,  $MgO$  1.84,  $SO_3$  1.96,  $S$  0.02, loss on ignition 2.20, insol. 0.05% was agitated in a fine condition with distd.  $H_2O$  of cond.  $5.07 \times 10^{-6}$  at  $25^\circ$  for a long period with exclusion of  $CO_2$ . The product was then filtered, analyzed, and the  $CaO$  content of the  $H_2O$  phase plotted as a function of time. At first the rate of soln. of  $CaO$  was very great, then for a considerable period the  $CaO$  content remained const. and suddenly increased again at a high rate, which diminished to become asymptotic to an equil. value. At first monocalcium silicate and tricalcium aluminate are extd. from the cement and hydrolyzed to form  $Ca(OH)_2$  at a high rate. The  $SiO_2$  and  $Al_2O_3$  gels thereupon ext.  $CaO$  from soln. and for a period these opposing rates are equal, the  $CaO$  content remaining const. This combination of  $CaO$  with the gel is physical adsorption and only after a long time does a chem. reaction occur to form a Ca aluminium silicate. The unchanged cement particles are surrounded by the gels which remain unchanged in the hardened cement. The equil. relation ( $CaO$  in the solid phase)/( $Ca$  in soln.) is, on account of this unchanged silicate, dependent upon the fineness of the particles. By expts. with varying fineness and by repeated extns. with  $H_2O$ , this ratio for the limiting case where all silicate is converted to gel was calcd. as approx. 7.

C. C. DAVIS

Variables in concrete from the construction standpoint. W. P. BLOECHER. *Eng.*

*World 22*, 170-4(1923).—With present-day refinement in design and application of concrete, the principal problem is how to get predetd. uniformity of strength. This can now be accomplished in the lab. with reasonable certainty; but field tests are commonly irregular and inconsistent. In the lab. the following may be controlled: (1) use of selected uniform materials (often artificially prepared) of known characteristics; (2) methods and app. of great precision; (3) protection from weather; (4) absence of the necessity for strict economy; (5) skilled permanent talent; (6) the relatively small magnitude of the physical operations. A list is given of 27 factors together with a range of their individual influence on the strength of typical 1 : 2 : 4 building concrete between the best and the worst conditions that may be encountered in practice. These include the quality of the cement, sand and coarse aggregate; grading of the aggregate; quantity and temperature of the mixing water; length of mixing time; curing conditions; condition of test cylinder when broken; and whether the cylinder was molded or drilled. Cores show no striking improvement in uniformity over molded cylinders. Judging concrete by 28-day cylinders may lead to unjust results; 60-day cylinders are often justifiable.

J. C. WITT

Tests of concrete in sea water. L. C. WASON. *Proc. Am. Soc. Civil Eng.* **48**, 1597-1604(1922).—The mech. action of the elements appears more important than the chem., while dry-casting of concrete work and the quantity of mixing water are influencing factors. Steel is adequately protected from corrosion, and a rich concrete made of good quality normal cement (or one low in alumina) mixed with 9-10% of water and dry-placed with careful spading gives durability below low and above high tides, enhanced if a protective coating is laid between tidal limits should abrasion be great.

J. S. C. I.

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Potash possibilities in Illinois [as by-product of the cement industry] (SCHROYER) **8**.

ISSEL, HANS: *Kunststein- u. Mörtelindustrie*. Leipzig: Bernh. Friedr. Voigt. 164 pp.

MARSH, CHARLES, and DUNN, WM.: *Manual of Reinforced Concrete*. London: Constable. 520 pp. 21s.

NASKE, CARL: *Die Portlandzementfabrikation*. 4th Ed. revised. Leipzig: Th. Thomas. 469 pp.

PROBST, EMIL: *Handbuch der Zementwaren- und Kunststeinindustrie*. 2nd Ed. revised. Halle a. S.: C. Marhold. 548 pp. M 290.

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Plaster or cement. H. S. THATCHER. *Can.* **228,860**, Feb. 20, 1923. Finely divided kieselguhr is mixed with finely divided calcined gypsum.

Hardening plaster, mortar or cement containing lime. J. PELC. U. S. **1,447,568**, Mar. 6. A mixt. of Na H sulfate and CaF<sub>2</sub> is added to accelerate hardening.

Waterproofing reagent for concrete. SET OKI. *Japan.* **40,198**, Oct. 4, 1921. Pptd. residue obtained from soy-bean oil is partly sapond. and BaCl<sub>2</sub> soln., kieselguhr and Al(OH)<sub>3</sub> are added. The product is dild. with H<sub>2</sub>O and used for mixing cement for concrete, etc.

Fibrous wall-board. J. H. CAFFEY. U. S. **1,447,708**, Mar. 6. A mat of loose fibers is coated with a liquid cement, the fibers are sepd. in places to form openings and the material is then compacted under pressure.

Coated roofing fabric. A. R. PURDY. U. S. **1,447,265**, Mar. 6. Threads are firmly embedded in the superficial coating while it is soft and sticky.

Preserving wood. W. H. JONES. *Brit.* **188,842**, Sept. 15, 1921. A compn. for preserving wood and destroying worms, etc., consists of coal oil (paraffin oil), white ppt., and naphtha, preferably wood naphtha.

**Preservative for timber.** MUNEMORI YOSHIMUNE and SHUICHI HONDA. Japan. 40,282, Oct. 11, 1921. Whale oil (18 l.) is sulfonated at room temp. After washing with  $H_2O$ , the sulfonated oil is combined with  $Cu(OH)_2$ , to which coal tar (180 l.) and camphor oil (18 l.) are added.  $Cu(OH)_2$  may be replaced with hydroxides of Hg or Zn. The reagent is soaked into the timber at  $130^\circ$ . It is sol. in  $H_2O$ , but insol. after soaking and exposing in the air.

## 21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

**John Ohlsson.** ALF. LARSON. *Teknisk Tids.* 53, *Almanna* 45-6(1923).—Obituary with portrait. Ohlsson contributed to the development of coal-tar products.

A. R. ROSE

**Modern utilization of fuels.** G. FRYSTER. *Z. angew. Chem.* 36, 117-9(1923).

E. H.

**Further data on the effective volatility of motor fuels.** R. E. WILSON AND D. P. BARNARD. *J. Soc. Automotive Eng.* 12, 287-92(1923).—A series of empirical curves is given by which it is possible by the aid of data from the distn. curve to det. the dew point of a non-aromatic fuel. Evidence is presented to show that the 85% distn. test is the best single measure for the effective volatility of a motor fuel from the standpoint of distribution and crankcase diln. The characteristics of 14 motor fuels are listed.

D. F. BROWN

**The coöperation of engineers in the chemical utilization of coal.** FRANZ FISCHER. *Anzeiger f. Berg., Hütten u. Maschinenwesen* 43, No. 40; *Chem. App.* 10, 17-9(1923).—When coal is coked at low temps. in a rotary furnace a porous, brittle half-coke results which is not suitable for fuel without further treatment. Expts. on a small scale have shown that if an Fe rod 8 cm. in diam. and nearly the length of the furnace is placed inside and crushed coal is charged into the rotary the rod squeezes the gas bubbles out of the plastic coal and results in a solid, uniform half-coke fit for fuel. The tar yield is the same as without the rod. Lab. expts. show that if the phenols in the tar are mixed with coke-oven gas and passed through galvanized Fe pipes at  $750^\circ$ , with close temp. control, 70% or more of the phenols will be converted into  $C_6H_6$ . In the presence of liquid  $H_2O$  at about  $200^\circ$  coal may be oxidized continuously to volatile and solid org. acids (and some  $CO_2$ ) by forcing air through it. All but the ash passes into soln., lime or soda being added to protect the steel app. against the acids formed. In these and many other processes it is the work of the engineer to devise app. suitable for large-scale operations.

J. H. MOORE

**Coal.** KANSHI KURIHARA. *J. Chem. Ind. (Japan)* 25, 131-58, 217-52, 420-42, 524-49, 673-91 (1922); cf. *C. A.* 16, 1143.—Past and present states of Japanese coal industry are reviewed. In order to promote the proper use of different varieties of Japanese coals, K. made extensive technical and chem. analyses of 175 typical samples collected from Japan, China, and Formosa. The methods of analysis for  $H_2O$ , volatile matter, ash, coke, S, N, calorific value, caking conditions and sp. gr. are given together with exact conditions under which each sample was collected. Except in a very few cases sp. gr. varies between 1.21 and 1.50; it is directly proportional to the ash content. When S is higher, however, ash is apt to be less, although sp. gr. is higher, because of the presence of heavy pyrite. Ordinarily with each increase of 1% ash, sp. gr. rises by 0.01. For the same type of coals, therefore, the ash content can be calcd. by  $A = (S - G) / 0.011$ , where G is sp. gr. of pure coal and S is sp. gr. of the coal. The  $H_2O$  content of the majority varies between 0.07 and 4.0%, which is considered as simple moisture. There are, however, some which ran above 10% which have characteristics near to that of lignite and in which  $H_2O$  must exist as inherent or combined according to Porter and

Ralston. Those contg. above 10%  $H_2O$  should not necessarily be classified as lignite. Eight tables are given. The analysis of volatile matter and caking properties show that the majority of Japanese coals belongs to non-caking coals. Those contg. volatile matter 45% or more have poor caking property, with rare exceptions; those with 45–40% have ordinary caking property, and are used as gas coals in Japan; those with 30–10% (semibituminous steam coal) and those less than 10% (anthracite) are very rare. Ash content varies between 2 and 30%. Eight typical samples were analyzed for  $SiO_2$ ,  $Al_2O_3$ ,  $Fe_2O_3$ ,  $CaO$ ,  $MgO$ ,  $Mn_2O_3$ ,  $SO_3$ ,  $P_2O_5$ ,  $K_2O$  and  $Na_2O$ , ( $SiO_2 + Al_2O_3$ ) + ( $Fe_2O_3 + CaO + MgO$ ), and m. p. Total S varies between 0.5 and 5.45%, pyritic S between 0.02 and 0.69%, sulfate S 0.01 and 0.11%, and org. S between 0.46 and 4.74%. N varies between 0.70 and 1.78% and is not above 2% as Anderson and Henderson's analysis of Japanese coal shows (0.84–3.40). Hard caking property, and  $H_2O$ , volatile matter, solid C, ash, S, N, calorific value of the cokes are also given. Most of the cokes contain 4%  $H_2O$ ; this depends on the adsorption power of the coal, which in turn depends on the coking temp. Volatile matter varies from 1 to 4%; most have 4%. The ash content of the cokes is discussed in detail. 13 tables are given. The effect of ash in coke on the different uses of coke is discussed. When coke ash is white, it indicates ordinarily a small Fe content. S in coke varies between 0.2 and 5.49%, existing as partly pyritic,  $SO_3$  and org. The chem. changes of different forms of S during dry distn. are considered.  $1/4$  of pyritic S volatilizes during distn. The higher the temp. used, the less becomes residual pyritic S. Most of the  $SO_3$  is reduced to sulfide, but this change does not affect the S content. Of org. S, the resinic S changes into more stable forms, and remains in the coke, while a part of the humus S volatilizes. The results of expts. on removing S from coke will be published later. A table shows the % of S in coals and cokes. Larger cokes contain lower S than smaller or granular cokes. The S contents of the more important Japanese cokes now on the market are given. N varies from 0.62 to 1.92%. Losses of N during dry distn. are given. They vary considerably with the kind of coal. Brown coal or the like loses more N than ordinary coal; anthracite contains the least amt. of volatile N. The other factors controlling loss of N during dry distn., such as type of oven, temp., speed of heating, are given. From 2 g. coal in an elec. oven during 30 min. 17–25% N is lost at 500°, 25–33% at 700° and 37–50% at 900°. Calorific values of coal and cokes are detd. and discussed. Direct detn. was made with Berthelot and Mahler's bomb calorimeter. The values vary between 4722 and 8300 cal.; calcd. on basis of pure coal they vary between 6301 and 9165 cal. The differences between these values and those calcd. from elemental analysis of C, H, O and S according to Dulong's formula are given for each coal. As an aid to classifying all the Japanese coals, an elemental compn. of the coal and calorific values are considered in detail. The literature bearing on various chem. compns. which are responsible for various types of coals is extensively reviewed. The amts. of C, H, O and org. S, N,  $H_2O$ , ash, volatile matter, solids, Frazer's ratio, and Dumble ratio are given. Classification of the different Japanese coals is attempted and discrepancy among classifications made according to the methods of Frazer, Grout and Dumble as applied to 175 samples of Japanese coals is considered. S. T.

Comparison between the American and South African methods for the determination of volatile combustible matter in coals. J. A. McLACHLAN. *J. S. African Chem. Inst.* 5, 6–11 (1922).—In the S. African method 1 g. of the sample is heated in a covered Pt crucible over a gradually increasing Bunsen flame until the sample ceases to give a flame at the lid, and the heating is then continued for exactly 30 secs. The Am. method consists in heating 1 g. of the sample in a covered Pt crucible over a full Bunsen flame for 7 mins., the size of the crucible, its height above the flame, and the size of the latter being definitely prescribed. At present it would seem that neither method yields con-

cordant results. Only one detail as regards the heating is specified in the S. African method, a fact which allows a wide variation in the results; the fuller specification in the case of the Am. method enables consistent results to be obtained when the detns. are made over one and the same burner, but different burners, having the same length of flame, have different heating values, and in this respect the method is defective. J. S. C. I.

**Spontaneous combustion of coals and lignites.** E. ERDMANN. *Brennstoff-Chem.* 3, 257-62, 278-83, 293-9(1922).—An historical survey is given. An attempt to test the liability to spontaneous combustion by treatment with ozonized air was unsuccessful. An app. was devised to measure relative initial combustion temps. (cf. Dennstedt and Schaper, *C. A.* 7, 1409). The sample (2-4 g.), in which was inserted the bulb of a thermometer, was placed in a glass vessel immersed in an oil bath, and a current of air or O preheated to the same temp. was passed through the sample. The bath was gradually heated until the temp. of the coal began to exceed that of the bath. The lowest (const.) temp. at which the coal must be heated in order that, when subjected to the action of a current of air or O, it should heat up ultimately to inflammation was taken as the initial ignition temp. Various factors governing spontaneous combustion of brown coals were studied by tests in this app. Increase in concn. of O<sub>2</sub> and O accelerated the ignition of the specimen. The inflammability was considerably increased when the size of the grains was diminished. When the moisture content of a coal was increased, its inflammability decreased. Wetting may, however, promote ignition in practice by removing the CO<sub>2</sub> which has collected in a pile and facilitating fresh access of O. Weathering was shown to diminish the tendency to ignition, especially of finely divided brown coal, which after 8 days would no longer ignite in cold ozonized O, while the ignition temp. in O was also raised. This effect of weathering is in contrast to that found by Dennstedt and Schaper. The inflammability was also reduced by maintaining the coal for some time a little below its ignition temp. The inflammability of various lignites and vegetable products was studied to identify, if possible, the active component. No connection with the % of C, H or O could be traced. It is a question rather of the kind of grouping. Unsats. compds. are a doubtful cause; polyhydric phenols are more probable active ingredients. The residue, after extn. of bitumen from lignites, is exceedingly prone to ignition. The practical conclusions arrived at are that excess of air and external sources of heat should be avoided, while provision of means of conducting heat away from storage heaps is beneficial. Wetting is not helpful, but a covering of wet fine coal which seals off the air is beneficial. CO<sub>2</sub> and flue gases may also be used for excluding air. The application of these ideas to lignite briquets is considered. J. S. C. I.

**Stone dusting of (coal) mines.** II. F. S. SINNATT, A. McCULLOCH, AND J. R. LOMAX. Lancs. and Cheshire Coal Research Assoc., *Bull.* 11, 27 pp.(1922).—The tendency of a coal dust to explode is proportional to the fineness of division of the dust. Thus a coal dust of 1/100 to 1/150-mesh ignited at 1350°, while the same coal ground to pass through a 220-mesh sieve ignited at 850°. The sensitiveness to inflammation is also inversely proportional to the % of volatile org. matter present in the coal, and there is a gradual transition from lignite to anthracite in this respect. The current required to ignite a sample of raw coal (1/200-mesh) was 11.5 amp., while to ignite the pyridine ext. a current of only 10.5 amp. was required, as contrasted with 15.0 amp. for the residue from the extn. It is a fallacy to believe that carbonate minerals such as limestone possess a greater effect in preventing explosions than other minerals of the nature of shale on account of their CO<sub>2</sub> content. The temp. at which the CO<sub>2</sub> is given off is too high for this action to take place sufficiently rapidly. The presence of moisture tends to prevent explosions of dusts, and expts. carried out in America have proved that the presence of 30% of water in any bituminous coal dust renders it practically non-explosive. It is, however, very difficult thoroughly to wet fusain, which may constitute 20-50%

of mine dusts. Fusain and ash have a retarding action on the liability of coal dust to explode. A quantity of 3 oz. of coal dust per cubic yard of air space is sufficient to cause a dust explosion. The least % of inert matter in mixts. with coal which will inhibit explosions is given as follows: for boiler ashes 57, quicklime 50, ground shale 43, Chance mud 38-40, gypsum 33-35, magnesia 28-30, anhyd.  $\text{Na}_2\text{CO}_3$  12-13, soda crystals ( $5\text{H}_2\text{O}$ ) 10,  $\text{NaHCO}_3$  9-10, and Glauber salt 8. Fine grinding of the inert material produces the most effective results as regards retarding explosions. The analyses of 7 shales are quoted, together with photomicrographs of inferior shale, mudstone, dust from inferior shale, shale suitable for stone dust, and dust prepd. from the latter shale. Results (unpublished) obtained by Sinnatt and Grounds on the weathering of shale are also quoted, in which it is shown that weathering facilitates the grinding of shale, and that artificial weathering, i. e., alternate heating and cooling, accelerates the breaking down of the shale to a greater degree than natural weathering. J. S. C. I.

**Suitability of different coals and vegetable matter for the preparation of activated carbon.** F. FISCHER, H. SCHRADER AND K. ZERBE. *Brennstoff-Chem.* 3, 241-4(1922).—The wash oil process in practice may still leave  $\frac{1}{3}$  of the benzene in the gas, but the use of activated C, though more effective, is too costly and the working life too short. Various raw materials have been examd. to see if supplies can be obtained so cheaply as to permit the discarding of the C after the activity has been impaired, e. g., by deposition of tar. A variety of vegetable substances and coals was examd. but only the lignites yielded a product comparable with that obtained from cellulose. The activity of the lignite coke could be improved by pressure extn. of the raw material with benzene. Alexandria lignite carbonized at  $800^\circ$  in steam yielded a coke capable of absorbing from air satd. with benzene 22.1% of its wt. as compared with 25.3% for charcoal from cellulose. J. S. C. I.

**Low-sulfur coal in Illinois.** G. H. CADY. Ill. State Geol. Survey, *Bull.* No. 38, 433-4(1922).—Extensive sampling has made possible the delineation of 2 areas of low-sulfur coal in the southern part of the state. The larger field is mainly in Franklin Co.; it is roughly  $10 \times 25$  miles in extent. L. W. RIGGS

**Sulfur compounds of coal, their behavior on distillation, and the sulfur compounds of coke.** J. P. WIBAUT. *Brennstoff-Chem.* 3, 273-8(1922). (Cf. *C. A.* 16, 1528, 2648).—The work of W. and others on this subject is critically reviewed. A method has been elaborated for distinguishing between pyritic S and org. S in coal and coke. When coal contg. both mineral and org. S was carbonized, the former was diminished, while the org. S content increased. The C apparently fixed some of the S given up by heated pyrites. The formation of C sulfides was confirmed by synthetic expts. starting from sugar charcoal and S, and they are regarded as similar to the "physico-chem. complexes" of C and O visualized by Rhead and Wheeler (*C. A.* 7, 2362) in their study of the absorption of O by C. The compds. are thermally very stable, and it seems improbable therefore that coke can be desulfurized on a mfg. scale. J. S. C. I.

**Economic firing of coal sludge.** F. EBEL. *Glückauf* 59, 88-91(1923).—Extensive data are given of boiler tests with coal sludge. C. C. DAVIS

**Artificial drying of peat.** G. KEPPELER. *Brennstoff-Chem.* 3, 237-9, 249-54, 262-9(1922).—Evapn. of the water from peat by artificial heat is impracticable, because the fuel requirement exceeds the calorific value of the product. It is conceivable that the evapn. might be effected in closed vessels with the production of steam from which an equiv. of power might be obtained, but this has not proved feasible in practice. The expression of the water is extremely difficult owing to the colloidal character of the peat, and the difficulty seems to increase as the peat ages owing to the breaking down of the cell structure which provided channels of egress for the water. K. and Raapke have shown that, given time, which is the dominating factor, most of the water can be

removed from the newer raw peat by pressure, but with an older specimen not even by prolonged application of the highest pressure could the water content be reduced below 75%. It is improbable that mech. expression or centrifuging of raw peat will prove effective. The removal of water is facilitated by admixt. of dry, powdery materials. The further dewatering is rendered much easier by admixt. of peat dried to 10–20% of water. By this means the bulk of the water can be removed from the peat by machines described in the paper. This "wet pressing" is regarded as the most promising process. Unsuccessful attempts have been made to facilitate the removal of water by addn. of electrolytes or liquids which have a greater wetting power than water. Freezing is effective if moss litter is required but the product is insufficiently coherent for fuel purposes. Similarly the preliminary application of heat facilitates subsequent removal of water as in the "wet carbonizing" process, though this has not established itself in practice. Electrosmose is effective, but owing to the small output per unit, has not proved commercially feasible. After surveying the whole field of artificial methods K. concludes that there is no immediate prospect that any will be successful and he concludes that the most promising field is the development of mech. appliances to facilitate the winning of peat to be dried in the normal way. J. S. C. I.

**The natural gas fields of Sarmasel.** L. LETSÖ. *Petroleum Z.* 19, 33–41, 61–7 (1923).—A detailed description of the geology of the field, methods of production and utilization, etc., with tables covering yield, analysis of the gas, costs of production, etc.

D. F. BROWN

**Recovery of sulfur from spent gas-purifying material by means of tetralin.** R. KATTWINKEL. *Brennstoff-Chem.* 3, 310–1 (1922).—Many solvents which have been proposed from time to time for the recovery of S from spent oxide either have been too dear or have given a dirty S owing to their solvent action on tarry substances. Tetralin, b. 203–5°, flash point 79°, dissolves 3% of its wt. of S at normal temps. and 40% at 100°. On this account, by careful cooling, the S can be produced in the form of fine crystals, all tarry matter being left in the mother liquor. The S recovered is clear yellow and cryst., burning without residue, and melting in an open tube at 119°. After extrn., the mass is treated with hot air to vaporize any tetralin, and is then ready for further use. J. S. C. I.

**Fall River gas plant.** A. C. KLEIN. *Am. Gas Assoc. Monthly* 5, 183–91 (1923). E. H.

**Experimental plant for producing benzene from phenols.** F. FISCHER, H. SCHRADER AND K. ZERBE. *Brennstoff-Chem.* 3, 289–92 (1922).—The app. was constructed to study on a larger scale the reduction of phenols by H to benzene and homologs (cf. *C. A.* 15, 162,590). The gas was satd. with vapor in passing through a vessel contg. heated phenols and thence passed into an iron tube coated internally with tin. This tube was 3 m. long, 28 cm. diam., and could be heated in a special gas furnace to 800°. The gas and vapor leaving the tube traversed two condensers cooled by water and a freezing mixt., resp., and afterwards two vessels charged with activated C. The gas was metered before and after passing the app., which was capable of dealing with 12 kg. of phenol per hour. The volatile reaction products were recovered from the C by a current of superheated steam. The results obtained are to be published separately. J. S. C. I.

**Conversion of phenols of coke-oven tar and low-temperature tar into benzene in an experimental installation.** F. FISCHER, H. SCHRADER AND K. ZERBE. *Brennstoff-Chem.* 3, 305–7 (1922).—The semi-industrial plant described above was used to investigate whether results obtained on such a scale were comparable with those obtained in a lab. app. in which a 90% yield of benzene was obtained by reduction of phenols with H in a tinned iron tube. The quantity of phenol put through the plant varied from 220



to 12,300 g. per hr., and the velocity of the H varied from 8 to 99 l. per hr. correspondingly. The crude benzene obtained, b. 80–100°, varied from 50.9% of the theoretical yield, with 815 g. of cresol mixture per hr., to 81.7% with 3100 g. per hr. Coal gas was used in one expt. in place of H, the yield obtained being 73.0% of the theoretical, but there was a slight sepn. of C.

J. S. C. I.

**Benzene from lignite.** F. FISCHER AND H. SCHRADER. *Brennstoff-Chem.* 3, 307–10 (1922).—The authors, continuing the work described in the preceding abstr., find that almost 50% of the wt. of phenols from lignite tars can be reduced to benzene by means of H. The benzene is mixed with other substances boiling at temps. up to 180°. The calorific value of benzene is about 10,000 cal./g., while that of phenol is only 7800 cal./g., so that for equiv. calorific values 78 g. of benzene corresponds to 100 g. of phenol. The phenols are derived from the humus portion of the coal, and while in gasworks benzene is formed direct in the retorts, in low-temp. operations it must be produced by reduction of the phenols occurring in the tar.

J. S. C. I.

**Phenols of low-temperature tars.** A. WEINDEL. *Brennstoff-Chem.* 3, 245–9 (1922). (Cf. C. A. 14, 1432.)—The tar acids from low-temp. tar produced in the Dellwik-Fleischer "Trigas" process have been examd. with a view to their identification. The tar acids were sepd. and fractionated within close limits. The C and H contents of these fractions were compared with the figures for known phenols. The low H contents point to the presence of unsatd. and polyhydric phenols. An alternative method was the detn. of the mol. wts. of the phenol acetic esters, which gave confirmatory results.  $\beta$ -Naphthol was identified.

J. S. C. I.

**Low-temperature coking in the inclined rotatory furnace.** A. THAU. *Glückauf* 59, 29–35, 55–64 (1923).—An illustrated description of the processes and equipment now being most used in Germany. Considerable data are given of analyses, yields, heat economy, and power consumption for furnaces at the Gelsenkirchen Bergwerk A. G.

C. C. DAVIS

**Recovery of pyridine from coke ovens.** W. CLAUD AND G. SCHNEIDER. *Ber. Ges. Kohlentechn.* 1921 (2) 93–111; cf. C. A. 16, 2981.—Pyridine suitable for denaturing alc. can be obtained from crude benzene recovered in coke-oven works, by extn. of the first runnings with  $H_2SO_4$ . The pyridine- $H_2SO_4$  should contain at least 20% of pyridine bases boiling under 160°, and be practically free from resins and oils, free from other acids and salts, such as HCl and sulfates, and practically free from iron salts. The analysis of the pyridine- $H_2SO_4$  is carried out by evapg. 500–1000 g. for  $\frac{1}{2}$  hr. on the water bath, cooling, and making alk. with 25%  $NH_4OH$ . The crude bases are sepd. and distd. up to 170°. The distillate is dried with solid NaOH, sepd. and re-distd. The wt. of bases passing over below 160° is detd.

J. S. C. I.

The structure and formation of humic acids and of coal (MARCUSSEN) 10. Rotary inclined horizontal drying drums (for coal) (U. S. pat. 1,447,929) 1.

WINTER, H.: *Wärmelehre und Chemie für Kokerei- u. Grubenbeamte.* Berlin: Julius Springer. 209 pp.

**Liquid fuel.** \* F. N. NICHOLLS and D. BROWN. *Brit.* 188,469, Sept. 22, 1921. Peat is steeped in  $H_2O$  and allowed to stand while a fungoid growth takes place; it is then kiln-dried, crushed and mashed in a mash tun. The liquid ext. is then fermented with yeast, etc., and distd. The distillate may be used by itself or mixed with a product obtained by distg. colza oil at a pressure of 8 atms. and a temp. of 600° F. The colza oil distillate may be replaced by a product obtained from the rape oil plant by steeping in  $H_2O$ , distg. in a tar or like still at about 6 atms., and redistg. at about 200–300° F.

**Liquid fuels containing colloidal carbon.** L. W. BATES. U. S. 1,447,008, Feb. 27. Petroleum fuel oils are associated with colloidal C derived from powd. coal or the like and maintained in colloidal condition by the action of coal tar, creosote and lime rosin grease, etc. Powd. coal of larger than colloidal size may also be associated with the fuel.

**Metaldehyde.** ELEKTRIZITÄTWERK LONZA. Brit. 189,074, July 18, 1922. Metaldehyde is stabilized for use as a fuel by the addn. of small quantities of  $(\text{NH}_4)_2\text{CO}_3$ .

**Carbonizing fuel in vertical retorts.** A. McD. DUCKHAM. U. S. 1,447,839, Mar. 6. Material such as coal which is to be carbonized is introduced into a vertical retort and alternately treated with a mixt. of O and N contg. N equal to or less than 40% the vol. of the O and with steam, introduced into the lower part of the retort, to produce a good yield of water gas and economical heating.

**Washing coal.** L. H. DIEHL. Brit. 188,325, Oct. 28, 1922. Coal is sepd. from gang by a flotation process which is carried out in a vacuum. The mixt. of coal and  $\text{H}_2\text{O}$ , to which floating media such as electrolytes, acids, or alkalies may have been added, is introduced by means of the pipes into the double conical sepg. vessel. A suitable construction is specified.

**Low-temperature distilling apparatus for coal.** HACHIRO SAITO. Japan. 40,199, Oct. 4, 1921. Coal is charged into a revolving tube, which is placed obliquely in the furnace and its inner surface has many projections fixed parallel to the axis or spirally. The flue is so constructed that the flame can heat the tube spirally and both ends of the tube are connected to the fixed part through flexible tubes.

**Distilling apparatus for brown coal.** KAZUO TATSUZAWA. Japan. 40,317, Oct. 18, 1921.

**Fuel feeder for destructive distillation retorts.** A. C. MICHIE and E. G. WEEKS. U. S. 1,447,680, Mar. 6.

**Carbon.** A. M. HART. Brit. 188,807, Aug. 24, 1921. Peat, lignite, sawdust, or other carbonaceous material, is preliminarily treated with a K or Na salt such as carbonate, chloride, sulfate, acetate or phosphate, either by wetting the material with a soln. of the salt, or if already wet by intimately mixing with the salt dissolved in the least possible amt. of  $\text{H}_2\text{O}$ , and is then carbonized by roasting the mass on a hot plate while freely exposed to the air. According to an example  $\text{Na}_2\text{CO}_3$  or soda crystals are employed. To obtain a pure C the product is boiled with dil. HCl and dried. The C produced may be worked up into briquets for fuel by the use of a binder such as gluten, molasses, or casein treated with HCHO.

**Gas.** W. BESWICK and N. E. RAMBUSH. Brit. 188,607, Feb. 21, 1922. In a gas-producer the whole or part of the gases generated is carried to pass through a considerable depth, say 14 ft., of fresh fuel which is thereby distd. in stages and at low temp. so that the gases leaving the upper part of the producer have a temp. of between  $150^\circ$  and  $300^\circ$  and a calorific value of about 170 B. t. u., high yields of  $\text{NH}_3$  and low-temp. distn. products being obtained. The temp. of the upper fuel zone may be controlled by removing part of the gases generated in the lower part of the producer prior to their reaching the upper zone. A central gas off-take comprises a bell situated near the top of the upper zone so that the ascending gases are distributed evenly over the cross-sectional area of the descending column of fresh fuel.

**Gas from powdered coal.** NOBORU KISHI. Japan. 40,322, Oct. 18, 1921. Finely powdered coal is heated with superheated steam at about  $300^\circ$  and when the coal is at the point of decompn. the mixt. is rapidly introduced into a furnace for incomplete combustion with hot air. Thus the coal is changed into gas mainly composed of CO. The construction of the furnace is given.

**Tar separator for purifying gas.** A. ROBERTS. U. S. 1,447,226, Mar. 6. Coke. BARRETT CO. Brit. 188,307, Sept. 4, 1922. A hard tough coke, suitable

for use as electrodes or in metallurgical processes, is obtained by coking coal tar pitch or pitch from oil-gas or water-gas in a beehive oven. The oven, which should have a level floor, is charged and heated by combustion of the volatile products which pass out and burn at the top so that a temp. of about 1400° F. is obtained, and when coking starts the temp. is raised to about 2200° F.; the coke is being quenched with H<sub>2</sub>O while still in the oven.

**Manufacture of coke.** KURAJI TAKEYAMA. Japan. 40,207, Oct. 5, 1921. Brown coal (or ordinary coal or wood) is incompletely burned. When the combustion is almost completed, about  $\frac{2}{3}$  of the material is drawn out from one end of the furnace and new material is charged. Thus the process is repeated.

**Burning powdered coke with more volatile fuel.** R. A. LIPSCOMB. U. S. 1,447,392, Mar. 6. Sufficient bituminous coal, culm, gas or other highly volatile fuel is blown into a burner together with finely divided particles of coke to ignite the latter by its combustion.

**Coke oven.** HACHIRO SAITO. Japan. 40,200, Oct. 4, 1921. The oven is divided longitudinally into charging, preheating, carbonizing, cooling, and quenching chambers. The chambers except the carbonizing one are filled with the waste gas to prevent the entrance of air. Along the side walls of the cooling chamber, preheating chambers for air are constructed and along those of the carbonizing chamber, combustion chambers for gas.

## 22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**Oxidation of petroleum hydrocarbons.** W. V. PIOTROWSKI AND W. JAKUBOWICZ. *Petroleum Z.* 19, 5-9(1923).—A review of the methods of sepn. of aromatic hydrocarbons from aliphatic compds. Boryslaw crude petroleum of sp. gr. 0.858, cold test 16° and paraffin content of 9.3%, as detd. by the Zalozieki method, was fractionated 3 times in a Glinski app. and 10-cc. fractions were collected. The aromatic hydrocarbon content in each fraction was detd. by the Hess app. and by nitration. The Hess method gave results 40-47% lower than the nitration method. Certain of these fractions passed over MnO<sub>2</sub> as a catalyst in an iron tube at 550-600° showed a large yield of unsatd. hydrocarbons, which by the Hess method were detd. as aromatics but on further analysis proved to contain only small amts of these hydrocarbons. The fraction boiling between 60° and 150° is almost entirely converted in this way into unsatd. compds. The catalyst influences the product formed and catalysts may be chosen by which large yields of aromatic hydrocarbons may be obtained. D. F. BROWN

**Proper utilization of natural gasoline.** L. F. BAYER. *J. Soc. Automotive Eng.* 12, 273-5(1923).—The production of natural gasoline is about 10% of the total gasoline production and this is about the max. % which should be used in blending with other gasoline to produce a satisfactory motor fuel. The 85% distn. test is now a better standard than the end point test for motor fuel. D. F. BROWN

**Fuel-oil experiences in the navy.** SCHULTZ. *Petroleum Z.* 19, 122-4(1923).—A description of fuel-oil burning in the German Navy. Mazut was found to be the best fuel. English, German and U. S. specifications are discussed. D. F. BROWN

**Influence of low temperatures on mineral oils in transformers and switches and the cold test for oil.** G. BRÜHLMAN. *Petroleum Z.* 19, 67-72(1923).—The importance of the cold test for transformer and switch oils is discussed and a modification of the Holde method of making the cold test is described. D. F. BROWN

**New oil fields of the Los Angeles Basin, California.** R. ARNOLD AND W. LOEL. *Oil Eng. & Finance* 3, 255-9(1923).—The geological formations of the 3 principal pro-

ducing areas are described. Commercial quantities of oil are confined to the Miocene and Pliocene formations.

D. F. BROWN

**Oil shale—Historical, technical and economic study.** M. J. GAVIN. *Bur. Mines, Bull. No. 210*, 201 pp. (1922).—Descriptions are given of foreign deposits of oil shale and of U. S. deposits. The nature and origin of oil shales, including analyses of mineral content, and the nature of the destructive distn. of oil shale are discussed. The history of the oil-shale industry is outlined and the development of the Scotch industry is given in detail. Present status of the industry in U. S. is discussed. The economic importance of the oil-shale industry to the U. S. is outlined. Types of retorts used in the U. S. are given. The problems of the industry are outlined fully with suggestions for solving some of them. Chapters are included under such heads as The Future of the Oil-Shale Industry in the U. S., Estimate of Costs and Profits in the Industry, Sampling and Assaying of Oil Shale, Physical and Chemical Data on Colo. Oil Shale. A bibliography on oil shale is included.

R. T. GOODWIN

**Oil shale and its utilization.** G. VON EMERICK. *Glückauf* 59, 113-20 (1923).—The occurrence, properties and distn. of oil shale are reviewed, with a description of past methods of gasification.

C. C. DAVIS

**Illinois bituminous shales.** N. O. BARRETT. *Ill. State Geol. Survey, Bull. No. 38*, 441-60 (1922).—The shale deposits of 9 counties are described. The results of analysis and of distg. tests are shown for over 20 samples of shale and several each of gas and oil. The oil or tar ranged from 0 to 48.8 gal. per ton. An av. would be misleading but of 18 samples that yielded some oil, 5 gave 36.0-48.8 gal. per ton; 6 yielded 11.6-16.4; and 7 yielded 0.5-4.5 gal. per ton. Some of the samples which gave but little tar or oil yielded much gas. Generally less than 1% of bitumen was extd. by solvent benzine, showing that distn. is the only method of obtaining the bitumen content.

L. W. RIGGS

**Chilian oil shale.** ANON. *Oil Eng. & Finance* 3, 253-5 (1923).—Analysis of 19 samples of shale from near Pular, Chile, showed an oil content of 12-14.5%. The oil as distd. has a sp. gr. of 0.934 which sinks to 0.887 on standing. Distn. tests show 8% over below 100°, 12% between 100° and 150°, 18% between 150° and 200°, 20% between 200° and 250°, 38% between 250° and 300° and 4% of a pitch residue. On mixing all the fractions below 200° and redistn. over CuO, a pale yellow oil of fragrant odor was obtained which did not deteriorate in 3 mos. S in the original oil is less than 2.25%. The paraffin content is about 10-12%.

D. F. BROWN

**Organic matter in oil shales.** R. H. MCKEE AND R. T. GOODWIN. *Ind. Eng. Chem.* 15, 343-9 (1923).—The carbon-hydrogen ratio in Colo. shale is 6.7 : 1 and the oil distd. therefrom by vacuum distn. 5.5 : 1. Thus the lower the yield of oil from a given shale which is completely carbonized, the higher may be the % of saturates in the oil. If the shale is heated slowly, the yield of oil is less, but its % of satd. compounds is increased. The nature of the oil produced is largely dependent upon the method of retorting. Diff. shales have different decompn. temps. and the reaction is both endothermic and exothermic. Curves give this difference in thermal decompn. temps. The action of several solvents on shale was detd. It is not commercially possible to ext. oil from shale with solvents for the oil is not present as such in the shale. The formation of oil is through an "intermediate product" that has been isolated. The formation is as follows: kerogen → "intermediate product" → shale oil. In contrast with the formation of unsaturates from petroleum by cracking, vacuum distn. of the shale yields a highly unsatd. "intermediate product" which is largely converted into satd. compds. by distn. under atm. pressure. For a more complete report on examn. of org. matter in oil shale by the same authors (cf. *Colo. School of Mines Quart.* 18, No. 1, Sup. A. (1923)).

R. T. G.

**New rotary shale retort.** ANON. *Chem. Age* (N. Y.) 31, 9-10(1923).—A retort designed by J. B. Newbery is described. A 5-ton retort gave  $3\frac{1}{4}$  bbl. of oil per day from a shale with oil content of  $27\frac{2}{3}\%$  gals. per ton. The retort consists of a number of shelves arranged one above the other; the heated shale is carried by arms through a complete revolution on each shelf and then falls through a slot to the next shelf. The heating is through a center flue.

R. T. G.

**Distillation of oil shale at Puertollano, Spain.** E. A. RITTER. *Eng. Mining J.-Press* 115, 326-7(1923).—The shale is mined at a depth of 300 ft. It is crushed to  $1\text{--}2\frac{1}{2}$  in. and distd. in retorts with a capacity of 4 tons in 24 hrs. A 6-ft. vein gives an average yield of 30 gals. per ton. The Scotch (Oakbank) type of retort is used; it consists of an upper part of iron construction  $11\frac{1}{2}$  ft. high and a lower portion of brick  $14\frac{1}{2}$  ft. high.  $(\text{NH}_4)_2\text{SO}_4$  produced is sold as fertilizer. Other products are kerosene, lubricating oil, phenols and paraffin oil.

R. T. GOODWIN

**Absorption of paraffin.** H. BURSTIN. *Petroleum Z.* 19, 119-22(1923).—Boryslaw crude oil was filtered through floridin and other absorbents such as kieselguhr. In every instance the paraffin content of the filtrate was less than that of the crude oil and the m. p. of the paraffin was raised. To prove that the rise in m. p. of the paraffin was not due to sepn. of asphaltic substances, a test was run on  $\text{H}_2\text{SO}_4$ -treated crude oil; the results were the same. There is a fundamental difference in the paraffin absorption itself between crude oil and distd. oil.

D. F. BROWN

**Determination of volatility of oils (MATTHIS) 27.** Physical and chemical properties of oil-country tubular material (SPELLER) 9. Drying and separating gases (Brit. pat. 188,666) 13.

BELL, H. S.: **American Petroleum Refining.** New York: D. Van Nostrand Co. 456 pp. \$5.

THOMSON, J. H. and REDWOOD, BOVERTON: **Handbook on Petroleum.** 4th Ed. Revised and enlarged by A. Cooper-Key. London: Charles Griffin & Co. 342 pp. 12s. 6d. Reviewed in *Chem. News* 126, 157(1923).

**Extracting hydrocarbon from shale or wood.** PLAUSON'S (PARENT CO.), LTD. Brit. 188,686, May 17, 1921. Shale, wood, etc., are treated *in vacuo* with superheated steam or an inert reducing gas or a mixt. of these at high temp. to recover hydrocarbons or turpentine and resin oil. A suitable construction is specified. Cf. 155,834.

**Fractional condensation and absorption of oil vapors.** J. C. BLACK. U. S. 1,447,118, Feb. 27. A desired fraction, e. g., naphtha, is recovered from mixed oil vapors obtained by distn., (e. g., distn. of petroleum oil) by the action on the vapors of a continuously circulating liquid of substantially the same compn. as the fraction which it is desired to sep. from the vapors treated.

**Purifying and distilling crude naphtha.** G. E. WALKER. Brit. 188,402, Aug. 11, 1921. In a continuous process for purifying crude naphtha and sepg. the constituents, the naphtha is distd. from stills heated to  $200\text{--}250^\circ$ . The vapors pass through columns and coolers. A suitable construction is specified.

**Manufacture of hydrocarbon oil from fatty oils or acids.** SHU SHIMIZU AND THE NIPPON GLYCERINE KÖGYÖ KABUSHIKI KAISHA. Japan. 40,210, Oct. 5, 1921. "By heating soaps (obtained from oil and fat or fatty acids by treating with alkali or alk. earth hydroxides) at  $450\text{--}550^\circ$  under ordinary pressure, light hydrocarbons are produced; fuel gas, C and carbonates are also produced as by-products. The yield of the light hydrocarbon is about 70-80% of the fatty acid; about 25% boiled under  $150^\circ$ , 57% at  $150\text{--}350^\circ$ , and 18% above  $350^\circ$ . With Fe, Ni,  $\text{AlCl}_3$ ,  $\text{Fe}_2\text{O}_3$ , or  $\text{NiO}$  as catalyzer in the heating, the quantity of gasoline in the product is increased above 30%.

**Concentration of sludge acid.** WM. A. SLATER. Can. 228,727, Feb. 13, 1923. Weak sludge acid from petroleum refineries is passed in countercurrent against a current of heated air to oxidize the impurities and conc. the acid. App. is also specified.

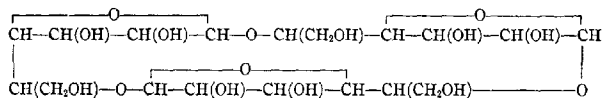
**Apparatus for extracting and distilling hydrocarbons from oil shale.** D. T. DAY. U. S. 1,447,296, Mar. 6. The app. is adapted for the combined extn. of oil from shale, employing both solvent treatment and distn. U. S. 1,447,297 relates to immersion of shale in an oil bath, then sepg. the solids from the bath, subjecting them to distn. and passing the vapors thus produced into the oil bath to serve for further extn. of shale.

**Bitumen.** H. BURNIE. Brit. 188,354, July 4, 1921. Bitumen is prepd. by distg. crude oils in the presence of a little  $\text{CaCO}_3$  to a temp. not exceeding  $274^\circ$  and heating the residue to  $250^\circ$  with S. Or a mixt. of crude oil, S, and carbonate may be distd. up to  $250^\circ$ . Natural bitumen may be hardened by heating to  $250^\circ$  with S. Cf. 3026, 1892.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

**Chemistry of cellulose.** J. C. IRVINE, W. S. DENHAM AND E. L. HIRST. *Chem. Trade J.* 71, 291 (1922).—Repetition of Denham's work on the methylation of cellulose (*C. A.* 8, 243; 9, 203), in which the methylation was repeated 20 times, gave a cellulose contg. 43% MeO, as compared with a theoretical value of 45% for a  $\text{Me}_2$  deriv. As the material preserved a fibrous structure there seems little likelihood that profound mol. alteration had taken place. Hydrolysis, by heating with 1% MeOH-HCl at  $125\text{--}30^\circ$  for 50 hrs., gave trimethylmethylglucoside (the last fraction contained a little dimethyl deriv.), the total yield being 90%. The pure fractions gave cryst. 2,3,6-trimethylglucose. In developing a formula one glucose mol. must be considered to account for the formation of cellobiose. The present difficulty is the variable yield of cellobiose obtained from cellulose. A sym. *tri-1,5-anhydroglucose* is proposed for the unit of cellulose on the ground that this structure would give a 70% yield of cellobiose as the theoretical max.



C. J. WEST

**Determining the degree of disintegration of cellulose.** HELMER ROSCHIER. *Pappers och Trävarutidskrift* 1922, No. 7, 108-12; *Zellstoff u. Papier* 2, 184-6 (1922); *Paper Trade J.* 76, No. 10, 49-50 (1923).—The rate of decolorization of 0.01 N  $\text{KMnO}_4$  contg. about 2.5%  $\text{H}_2\text{SO}_4$  by cellulose is a measure of the degree of disintegration of cellulose. Very hard sulfite decolorizes the soln. in approx. 25 sec.; ordinary hard, 25-35; medium hard, 35-50; hard-bleaching 50-70; easy-bleaching, 70, all expts. being carried out at  $20^\circ$ . With increasing temp. the time is decreased. The relation to Sieber's Cl no. is shown by table and curves

C. J. WEST

**Theory of the solvent action of aqueous solutions of neutral salts on cellulose.** H. E. WILLIAMS. *Mem. Proc. Manchester Lit. Phil. Soc.* 65, part XII, 1-14 pp. (1921).—The soln. of cellulose in an aq. soln. of a neutral salt is independent of the chem. nature of the salt but is largely dependent upon the physical properties of the salt soln. For such a soln. to dissolve cellulose it must consist of a liquid hydrate—an associated mol. complex of salt and  $\text{H}_2\text{O}$ . But this complex must be of such an order that it has a viscosity above a certain min. and a positive heat of diln. between well defined limits. These limiting conditions will vary according to the nature of the cellulose and the

treatment which it has previously undergone; but for any particular cellulose the limits will be const. for all salt solns. in  $H_2O$ .

**Determination of cellulose in plant material according to the method of Cross and Bevan.** RUDOLF SIEBER. *Zellstoff u. Papier* 3, 27-9(1923).—In the detn. of cellulose according to Cross and Bevan there is uncertainty in recognizing the end point of the reaction; consequently the cellulose is liable to be attacked. A method is described whereby the reaction is interrupted, yielding an unattacked cellulose. The chlorination app. consists of a wide glass ring over the bottom of which is drawn and tied a linen cloth filter. It is of a size to fit a 6-cm. Buchner funnel. A rubber ring is inserted between the funnel and the bottom edge of the glass container to insure good suction. 3 to 4 g. wood meal is placed in the app. and heated in a beaker contg.  $H_2O$  thoroughly to moisten the sample; after cooling, the  $H_2O$  is sucked off, and a satd. soln. of  $Cl-H_2O$  added. With the disappearance of the  $Cl$  odor (5 to 10 min.) the liquid is sucked off to remove the  $HCl$  formed and washed once. The treatment is repeated until the residue is nearly free from lignin. After washing, the residue is accorded the usual treatment with  $Na_2SO_3$  soln., first for 30 min., then for 20 min., washed, transferred to a Gooch crucible, dried and weighed. In an actual test the total chlorination time was 30 min. and 200 cc.  $Cl-H_2O$  were used. The corrected  $Cu$  no. of the isolated cellulose was never above 1.5 and there was no evidence of oxycellulose. This residue can be further investigated, by known methods, for its content of lignin and pentosans.

J. L. PARSONS

**An improved method for the determination of  $\alpha$ -,  $\beta$ - and  $\gamma$ -cellulose.** M. W. BRAY AND T. M. ANDREWS. *Ind. Eng. Chem.* 15, 377-8(1923).—The sample of cellulose or pulp is extd. with 17.5%  $NaOH$ . The insol. portion ( $\alpha$ -cellulose) is filtered, dissolved in 72%  $H_2SO_4$  and titrated with standard  $K_2Cr_2O_7$  soln. The alk. filtrate is divided into two portions, one of which is titrated with standard  $K_2Cr_2O_7$  soln. ( $\beta$ - and  $\gamma$ -cellulose), while the other is acidified with 10%  $H_2SO_4$ , which ppts. the  $\beta$ -cellulose and is then titrated with standard  $K_2Cr_2O_7$  soln., which gives the  $\gamma$ -cellulose. The difference between the last 2 values gives that for  $\beta$ -cellulose. The method of standardization of the  $K_2Cr_2O_7$  against cellulose obtained by the chlorination method of Cross and Bevan from sulfite pulp is given.

C. J. WEST

**Analytical methods for the control of chemical operations in soda and sulfate pulp mills.** RUDOLF SIEBER. *Papierfabr.* 21, 89-94(1923); cf. *C. A.* 17, 634.—This is chiefly a review of recent improvements in analytical methods written in anticipation of the report of the German Analysis Commission for Soda and Sulfate Mills. The following subjects are covered: raw materials, cooking liquors, cooking process, pulp, lime sludge, and by-products as turpentine and  $MeOH$ .

J. L. PARSONS

**Composition of chemical pulps of various origins.** JULIEN. *Papeterie* 45, 117 (1923).—Analyses are given of (1) bleached Austrian sulfite, (2) No. 1 strong German sulfite, (3) No. 2 strong German sulfite, (4) "St. Lawrence" Canadian easy bleaching sulfite, (5) "St. Lawrence" Canadian hard sulfite (6) "Ha Ha Bay" Canadian sulfite, (7) unbleached Scandinavian sulfite, (8) unbleached Scandinavian soda poplar. All detns. were carried out on bone-dry pulp, excepting ash, which was detd. on air-dry pulp. Lignin was detd. by Becker's 72%  $H_2SO_4$  method, resin (including fat and waxes) by extrn. with  $Et_2O$ ,  $\alpha$ -cellulose by means of 17.5 %  $NaOH$ , baryta resistance by the Schwalbe-Sieber method, and  $Cl$  no. by a modification of Sieber's method (details not given).

A. P.-C.

**Properties and uses of paper pulps.** ARIBERT AND REYMOND. *Mon. Papeterie française* 53, 566-7, 588-9(1922); 54, 13-4, 34-6(1923).—A description of rag (cotton, flax, hemp, ramie, jute and wool), ground-wood, sulfite, soda, sulfate, kraft, esparto, straw, bamboo, and reed pulps, and of waste-paper stock, of the effects of beating and

refining, and of the various parts of the paper machine and their respective functions.

A. P.-C.

**The treatment of cotton as a raw material for cellulose esters.** MAURICE FANJAT. *Papier* 26, 73-6(1923).—Brief description of the purification of cotton, both on a lab. and on a com. scale, covering sorting, dusting, cutting, defibering, boiling, bleaching, and drying.

A. P.-C.

**Rotten wood in paper making.** C. S. V. HAWKINS. *Pulp Paper Mag. Can.* 21, 287-9(1923); cf. Bates, C. A. 17, 1139.—Wood contg. approx. 12% (by vol.) of rotten wood gave 0.483 tons pulp per cord as compared with 0.542 tons from sound wood (sulfite); in the ground-wood process, 0.88 and 0.92 tons per cord were obtained. Although the yield by the sulfite process is lower, it is the better method of utilizing rotten wood, since the color and dirt cause very unsatisfactory results in ground wood.

C. J. WEST

**Relative strength of sheet-machine and hand-mold sheets.** F. SUTERMEISTER. *Paper Ind.* 4, 1661-2(1923).—The sheet machine will give sheets of practically const. wt. regardless of time of beating, within reasonable limits. There is no possibility of calcg. from the tests on hand-mold sheets what those on machine-made sheets would be. Wherever possible, the use of the hand mold for quant. work should be abandoned.

C. J. WEST

**Determination of mechanical wood pulp in printing paper.** H. KRULL AND B. MANDELIKOW. *Papierfabr.* 20, 1213-6(1922).—The detn. of the phloroglucinol absorption value, carried out exactly according to the method of Cross, Bevan, and Briggs (C. A. 1, 2942), affords a convenient and accurate measure of the % of mech. pulp in "news" and similar printing papers. In calcg. the results, however, the original factors 8 for mech. wood and 1 for sulfite pulp cannot be accepted as sufficiently accurate. The true av. values for these factors are 7.84 for mech. and 1.34 for unbleached strong sulfite pulps. The error involved by using the original factors is negligible for papers contg. between 65 and 75% of mech. wood pulp, but becomes very considerable in the case of papers contg. low percentages of that constituent. The corrected formula for calcg. the result, expressed on the dry substance, is  $H = 100(P - 1.34)/(7.84 - 1.34)$ , where  $H$  is the % of mech. pulp and  $P$  is the phloroglucinol absorption value of the paper.

J. S. C. I.

**The elasticity of latex paper.** A. D. LUTTRINGER. *Caoutchouc & gutta-percha* 20, 11701(1923).—According to tests at the Lepard & Smith paper mill (England), paper contg. latex showed 5-20% greater strength and 25-100% higher folding test than that without latex. Comparative tests of the elasticity of plain and of latex paper weighing 119 and 118.3 g. per m.<sup>2</sup>, resp., by means of a Breuil elasto-durometer were made by L. Paper contg. 1% latex gave av. values, based on the rebound of the steel ball, 3% higher than the plain paper.

C. C. DAVIS

**Pitch troubles in newsprint paper mills.** FREDERICK BARNES. *Chem. Met. Eng.* 28, 503-6(1923).—Ground-wood pulp is probably never the starting point of pitch troubles. This is more likely to be found in spruce wood but not in balsam or jack pine. Typical compn. of pitch is: solid grease and resin, 55%; soap and color, 8.7; inert pitch, 24.7; ash, 3.8; undetd. 7.8. Extn. tests (rosin-fat content) are reported for a no. of woods and for ground-wood and sulfite pulps. If the pitchy pulp be raised to temps. above 150° in the digester, pitch troubles on machines may be almost eliminated. Between 150° and 155° the previously fluid pitch shows a decided hardening of the resinous matter. Practical suggestions are given for avoiding this trouble.

C. J. WEST

**Wall paper manufacture in a model mill.** HERBERT A. HAUPTLI. *Chem. Met. Eng.* 28, 437-40(1923).—A general descriptive article.

C. J. WEST

**Composition of the rosin size emulsion.** N. D. IVANOV. *Bumazhnaia Promy.*



*shlenost* 1, 33-8(1922); *Paper Trade J.* 76, No. 11, 45-6(1923).—In order to det. the extent of hydrolysis of Na resinate, coagulation by freezing out and ultrafiltration were used. The *hydrolysis constant* for a soln. contg. 15.392 g. total rosin per l. of emulsion, was 0.662; for 5 g. per l., 0.847; for 0.5 g. per l., 0.922; in the most dil. soln. the size can be considered as completely hydrolyzed, giving a colloidal soln. of rosin in an alk. medium.

C. J. WEST

The effect of sunlight on the vegetable paper sizes. L. P. ZHEREBOFF. *Bumazh-naia Promyshlennost* 1, 25-32(1922); *Paper Trade J.* 76, No. 11, 50-2(1923).—All papers, irrespective of compn., lose in size fastness through exposure to light. The effect of the light becomes evident within 10 days; after 1.5-2 mo. all papers become slack-sized and after 0.5 yr. as if entirely unsized. The rays destroying sizing are violet, blue and yellow; green and red rays have little effect. The rapidity of the destruction of sizing indicates that the rosin, which det. the sizing of paper, is very susceptible to the action of light; *i. e.*, it is present as a very thin mol. film on the surface of the fibers.

C. J. WEST

Degree of dissociation and unsaponifiable matter in rosin size. A. HAUG. *Wochbl. Papierfabr.* 54, 313-5(1923); cf. *C. A.* 17, 1329.—The effects of small amts. of different salts of the alkali and alk. earth groups on solns. of Na resinate, at different concns. were studied. Solns. of Na resinate, contg. less than 10 g. of rosin per l. are pptd. by salts at an approx. concn. of 1 g. per l. Ca salts have a greater flocculation effect than Na salts. The effect of hard H<sub>2</sub>O on the compn. of rosin size is shown.

J. L. PARSONS

Cellulose acetate in the manufacture of artificial leather (DESCHIENS) 29. Piezo-micrometer and its applications to testing paper (STRACHAN) 1. A magnesyl derivative of cellulose (COSTA) 10.

Cellulose from reeds, etc. H. STEINHILBER. *Brit.* 188,828, Sept. 2, 1921. Addn. to 179,885 (*C. A.* 16, 3545). The process according to the principal patent is applied to the manuf. of cellulose from reeds, etc., such as Cyperaceae, Gramineae, and Typhaceae, and also to the treatment of the more resistant marrow cells or portions remaining after the crude fibers have been sepd. It consists in subjecting the product, during or subsequent to bleaching, to the mech. treatment consisting of a continuous rubbing and pressing action. In the treatment of the marrow cells, the material is first bleached and the cellulose fibers are then sepd. by continuously rubbing and pressing in the presence of H<sub>2</sub>O.

Viscose. H. GASSMANN. U. S. 1,447,465, Mar. 6. Coagulated viscose under tension is treated with a H<sub>2</sub>O-repellent substance such as heated oil to improve its durability.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

The speed of uniform movement of flame in mixtures of paraffins with air. WALTER MASON. *J. Chem. Soc.* 123, 210-4(1923).—This was detd. for mixts. of air with CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> and C<sub>5</sub>H<sub>12</sub>, resp., by the "photographic method" in a tube 5 cm. in diam by 2.4 m. in length and contg. 2 quartz windows through which the flame could be photographed on a moving film. This method is more accurate than the "screen-wire method" (*C. A.* 14, 1043), since it records only the "uniform movement," while the latter may record a part of the "vibratory movement" also. The data for a large number of mixts. of each of the hydrocarbons with air are given. The screen-wire

method is sufficiently accurate for most purposes and as a rule easier to employ.

CHARLES E. MUNROE

**Rapid method for determining acetone in smokeless powder.** M. MARQUEVROL AND P. LORIENT. *Mem. poudres* 19, 362-7 (1922).—The method depends on the formation of  $\text{CHI}_3$  when  $\text{Me}_2\text{CO}$  is treated with  $\text{NaIO}$  in the presence of alkali. The  $\text{NaIO}$  results from reaction between  $\text{NaClO}$  (eau de Javel) and  $\text{KI}$ . To standardize the  $\text{NaClO}$  soln., 10 cc. pure  $\text{Me}_2\text{CO}$  is dild. with  $\text{H}_2\text{O}$  to 1 l. and 10 cc. of this soln. dild. to 100 cc. To this, 10 g.  $\text{KI}$  and 20 cc.  $\text{NaOH}$  soln. ( $36^\circ\text{Bé.}$ ) are added and the mixt. is titrated with the  $\text{NaClO}$  soln., with an outside indicator (1 g. starch, 10 g.  $\text{NaHCO}_3$ , 100 cc.  $\text{H}_2\text{O}$ ). The end point is very sharp. To det.  $\text{Me}_2\text{CO}$  in smokeless powder, 20 g. of the powder, finely divided, is decomposed by gently warming for 1 hr. with 100 cc.  $\text{NaOH}$  ( $36^\circ\text{Bé.}$ ) and 500 cc.  $\text{H}_2\text{O}$  in a distg. app., then 450–480 cc. distd. into a 500-cc. graduate surrounded by cold  $\text{H}_2\text{O}$ . The distillate is made up to 500 cc., mixed and filtered. 100 cc. is treated with 10 g.  $\text{KI}$  and 20 cc.  $\text{NaOH}$  ( $36^\circ\text{Bé.}$ ) and titrated with the  $\text{NaClO}$  as above. Results are not affected by  $\text{EtOH}$ ,  $\text{MeCHO}$ ,  $\text{NH}_3$ , or  $\text{PhNH}_2$ , but substituted ureas, e. g., diethyldiphenylurea, give traces of  $\text{CHI}_3$  corresponding to 0.1–0.2%  $\text{Me}_2\text{CO}$ . Tabulation of results obtained on various samples of foreign powders shows  $\text{Me}_2\text{CO}$  varying from 0.13% to 2.03%. C. G. STORM

**Draining of (nitrocellulose) powder before drying.** L. BUTIN. *Mem. poudres* 19, 245-7 (1922).—A saving of steam and time in the final drying of "water-dried" smokeless powder was effected by removing as completely as possible the mechanically adhering  $\text{H}_2\text{O}$  from the powder grains as taken from the  $\text{H}_2\text{O}$  tanks. 40–50 kg. of powder is placed in a hexagonal drum with slotted sides 2 m. long  $\times$  0.6 m. wide, which is rotated once per sec. for several min. The  $\text{H}_2\text{O}$  content is thereby lowered 2% and the time of final drying reduced 8 hrs. C. G. STORM

**Increasing the capacity of the driers in the drying of smokeless powder.** (Poudre BG<sub>3</sub>). AB-DER-HALDEN. *Mem. poudres* 19, 339–44 (1922).—The usual method of only filling the driers to  $\frac{2}{3}$  capacity is without advantage. With the driers loaded to capacity, the increased concn. of  $\text{Et}_2\text{O}$  in the air did not, as had been feared, cause the strips of powder to soften and adhere to each other. The powder dried just as rapidly and the recovery of solvent was increased 7%. C. G. STORM

**The early stages of a submarine explosion.** H. LAMB. *Phil. Mag.* 45, 257–65 (1923).—A theoretical treatment of the expansion of a spherical cavity (with given initial radius) contg. a gas at a known high initial pressure in the midst of an unlimited mass of liquid initially at rest. Although many limiting assumptions are made in approaching the problem it represents the closest approximation now possible to the early stages of a submarine explosion. Assuming the liquid to be incompressible, equations are developed and solved for values which are plotted to show the rate of expansion of the gas. Boyle's law is first assumed and later the adiabatic law of expansion. If the compressibility of water be taken into account, the results will be considerably altered for high pressures (above 10,000 atms.). The accurate equation involving compressibility can be formulated but appears to be insoluble. An approx. treatment is presented. At a sufficient distance from the origin the ordinary theory of sound waves in water becomes applicable. S. C. L.

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The detonating action of  $\alpha$ -particles (POOLN) 3.

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**High explosive.** W. R. SWINY. *Can.* 228,858, Feb. 20, 1923. The compn. consists of cellulose nitrate 20–75, nitroglycerin 3–27,  $\text{NaNO}_3$  0–50, and water 3–15%. Cf. C. A. 16, 2030.

"Smokeless-powder dynamite." L. H. JONES. U. S. 1,447,248, Mar. 5. Ground

smokeless-powder 15-50 is mixed with  $\text{NaNO}_3$  0-40,  $\text{NH}_4\text{NO}_3$  6-67, TNT 1-15, nitroglycerin 0.25-2 and wood pulp 0-2 parts.

**Igniting mixture for small arms ammunition.** C. I. B. HENNING. U. S. 1,447,551, Mar. 6. An igniting mixt. which ignites without detonation when lightly struck is formed of tetranitropentaerythritol which may be mixed with  $\text{KClO}_4$ ,  $\text{Pb}(\text{CNS})_2$ , Sb sulfide or Hg fulminate.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

**New anthraquinone vat dyes.** HANS TRUTTWIN. *Z. angew. Chem.* 35, 702(1922).—Benzenesulfonylchlorides react with mononuclear aromatic amines giving sulfamines  $\text{RSO}_2\text{NHR}'$  (C. A. 9, 307); the condensation of aminoanthraquinones with aromatic sulfonylchlorides in  $\text{PhNO}_2$  does not form sulfamines (Medenwald, *Diss. Berlin*, 1911, Ger. pats. 224, 982, 227, 324) but gives compds. of uncertain constitution pptd. from the reaction mixt. by  $\text{Et}_2\text{O}$ , insol. in alkalies, giving vats with alkali and rongalite, and dyeing cotton fast shades, but low in tinctorial power; these indicate the possibility of a new class of vat dyes contg. S. 110 g.  $\beta$ -aminoanthraquinone (A), 100 g.  $\text{MeC}_6\text{H}_4\text{SO}_2\text{Cl}$  (B), and 500 cc.  $\text{PhNO}_2$  were boiled several hrs. under a reflux, the crystals sepd. on cooling were filtered off, and the filtrate was treated with  $\text{Et}_2\text{O}$  which pptd. a blue-black dye-stuff (C) insol. in alkali and giving a red vat with alk. rongalite, which dyes cotton fast, weak, dull violet-brown shades increased in intensity by a higher proportion of alkali such as is used for indanthrene colors, the dyestuff going into soln. better; boiling with soap lessens the color intensity. C is insol. in  $\text{CCl}_4$ , fairly sol. in  $\text{EtOH}$  or  $\text{AcOH}$ , sol. in concd.  $\text{H}_2\text{SO}_4$  with green-blue color and, reprecip. on diln., gives violet-brown solns. with  $\text{Me}_2\text{CO}$ ,  $\text{AcOEt}$ , or pyridine, and violet with  $\text{CHCl}_3$ ; it differs distinctly from Medenwald's product (Ger. pat. 227, 324). Analysis: N 4.33%, S 4.28%. The ditoluene deriv. is brown, with red color in  $\text{H}_2\text{SO}_4$ . 110 g. A and 9 (?) g.  $\text{PhSO}_2\text{Cl}$  (D) were heated with 50 cc.  $\text{PhNO}_2$ ; after treating as above,  $\text{Et}_2\text{O}$  pptd. a vat dye sol. in  $\text{H}_2\text{SO}_4$  with blue color, pptg. a violet compd. with  $\text{H}_2\text{O}$ , insol. in alkali, fairly sol. in  $\text{AcOEt}$  or  $\text{Me}_2\text{CO}$  with red-brown, sol. in  $\text{CHCl}_3$  with dirty greenish brown, easily sol. in pyridine with brown-violet, and in  $\text{AcOH}$  with violet color; analysis: N 5.04%, S 4.86%. 22 g.  $\alpha$ -aminoanthraquinone (E) and 20 g. B, heated in  $\text{PhNO}_2$  and treated as above, formed a vat dye sol. in  $\text{EtOH}$  or  $\text{AcOH}$  with brown color; analysis: N 4.52%, S 4.13%.  $\text{CCl}_4$  is less effective than  $\text{Et}_2\text{O}$  in pptg. the dyestuff. There were also prepd. dyestuffs from A with  $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$  (violet-brown); from indigo with B; (gray-blue); from A with D (gray); and from E with B (gray); the gray dyes may be technically important.

A. R. ALBRIGHT

**Modern equipment for dyeing, bleaching and finishing operations.** E. A. TURNER. *Am. Dyestuff Rep.* 12, 165-9(1923).

E. H.

**Sample dyeing.** P. HUC. *Halle aux cuirs* 1923, 21-5.—Discussion of the theory of color mixing and of a simple method for prepg. graduated color shades.

F. L. SEYMOUR-JONES

**Hyposulfites in dyeing silk and cotton with sulfur and vat dyes.** FRANK REMLEIN. *Am. Dyestuff Rep.* 12, 112(1923).—The advantages of the hyposulfite vat are compared with the older processes and special directions are given for its use in dyeing silk.

L. W. RIGGS

**The question, "What is the dyeing power (of a fiber)?"** ED. JUSTIN-MUELLER. *Chem.-Ztg.* 47, 91(1923); cf. Münz and Hayn, C. A. 17, 1552.—The dyeing power of a fiber, that is, its absorption, and particularly its retention, of a dyestuff is advantageously studied with the microscope, using 1200 X magnification. Level dyeings, fast to rub-

bing, appear as true, uniform, solid solns., completely transparent, resembling similar solns. in gelatin; uneven dyeings of colors not fast to rubbing appear turbid and irregular, *i. e.*, as imperfectly dissolved. Perfect dyeings are somewhat comparable with extns. with immiscible solvents, but while the solvents in the latter case are unaltered, the fiber must be in a hydrated, or "swelled" (turgid) condition, which is developed in different degree by various fibers, and which is responsible for different degrees of solvent power, or retentivity. Dyeing power is defined as "the power of the (swelled) fiber to dissolve and retain a dyestuff." If wool be treated with  $\text{Ac}_2\text{O}$  in the presence of  $\text{H}_2\text{SO}_4$ , it loses its colloid  $\text{H}_2\text{O}$  and turgescence as well, and dyed wool by the same treatment loses its color retentivity; wool so treated may be "re-activated" through hydration by several hrs. contact with 50%  $\text{H}_2\text{SO}_4$ , which produces a measure of hydrolysis as well, recognizable by the biuret reaction. Cotton behaves in a similar way (cf. Favre, *Ber. von Mülhausen i. E.*, 1912); its turgescence is greatly increased on treatment with glycerol, by which its retention of colloid  $\text{H}_2\text{O}$ , and of color, are improved (*C. A.* 7, 2310). Wetted fibers have in general a stronger affinity for the dyestuff, and greater resistance to agents which tend to reduce turgescence.

A. R. ALBRIGHT

**Dyeing of chlorinated wool.** J. R. ADAMS. *J. Phys. Chem.* 27, 81-4(1923).—Tables and curves show in detail that wool, previously treated with bleaching powder and dried after washing with HCl, adsorbs typical acid dyes in definite relation to the H-ion concn. of the dye bath; *Orange II* was adsorbed in the amt. of 83.3% of that started with, from a bath having  $p_H$  2.55, and to the extent of 1.03%, from  $p_H$  6.43; the 8 intermediate values shown are not far from linear. Acid  $\text{Na}_2\text{SO}_4$  in a soln.  $p_H$  3.05 had a stripping action affecting 47.1% of the dyestuff used; with  $p_H$  2.45, it was 32.3%. The effect with *Lake Scarlet R* was very similar, the limiting values of 10 detns. showing adsorption to be 95% for  $p_H$  2.73, and 1.73% for  $p_H$  5.76; the stripping effect of  $\text{H}_2\text{SO}_4\text{-Na}_2\text{SO}_4$  was 31.2% with  $p_H$  3.27, and 20% with  $p_H$  2.55. Each  $p_H$  value was detd. after the dyeing had been completed; cf. (Lewis, Brighton and Sebastian, *C. A.* 11, 3154); the final concn. of dyestuff in the bath was detd. by direct titration with  $\text{TiCl}_3$  (*Ber.* 36, 1552(1903); 40, 3819(1907)). The adsorption curves of chlorinated and of ordinary wool lie very close together; dyeings on the former are much brighter than on the latter, probably due to the increased glossiness of the chlorinated wool, and possibly to the presence of acid in the wool.

A. R. ALBRIGHT

**Use of dichromates as a mordant in dyeing.** W. C. DURFER. *Am. Dyestuff Rep.* 12, 91-5(1923).—The best fixation is secured by a min. of chrome. Org. acids are preferred to  $\text{H}_2\text{SO}_4$  in chrome mordanting. The special qualities of  $\text{KHC}_4\text{H}_4\text{O}_6$  in connection with chrome mordanting are described.

L. W. RIGGS

**Automatic control of time and temperature schedules in the dye kettle.** V. WICHUM. *Am. Dyestuff Rep.* 12, 106-10(1923).—The methods and advantages of automatic control are described.

L. W. RIGGS

**Uses of sulfoxylates in calico printing.** W. R. MCINTYRE. *Am. Dyestuff Rep.* 12, 110-1(1923).—The subject is discussed under the following heads: (1) discharge effects on colored ground, (2) printing vat colors (3) indigo discharges. The practical use of the sulfoxylates in these processes is described.

L. W. RIGGS

**The possibility of using phosphorescent substances in calico printing.** S. G. SHIMANSKI. *Ber. Polyt. Iwanowo Wosniessensk* 4, 171-2(1921).—Mixts. contg. phosphorescent sulfides have been used successfully, the fabric being printed with a paste contg. the sulfide,  $\text{NH}_3$ , and albumin. During printing, the fabrics must be protected from light, since the small quantities of  $\text{AcOH}$  formed cause decompn. of the sulfides. Unsatisfactory results were obtained with acid dyestuffs, *e. g.*, eosin and fluorescein.

J. S. C. I.

The vital resistance of ravaging insects of skins, furs and wools (RIGOR) 29. The

catalytic action of mercury in the sulfonation of anthraquinone (CLOUGH) 10. Dyes derived from diphenic anhydride (DUTT) 10.

FHRMANN, EDOUARD: *Traité des matières colorantes organiques et de leurs diverses applications*. Paris: Dunod. 615 pp. Fr. 58, bound Fr. 63.75.

HALL, A. J.: *Dyes and their Application to Textile Fabrics*. London: Sir Isaac Pitman & Sons, Ltd. 118 pp. 3s.

THORPE, J. F. AND INGOLD, C. K.: *Vat Colors*. Monograph on Industrial Chemistry. Edited by Edward Thorpe. London: Longmans, Green & Co. Printed in Saxony by Karras, Kröber and Nietschmann. 16s. Reviewed in *Chem. Trade J.* 72, 300(1923).

**Yellow azo dyes.** E. REBER. U. S. 1,447,485, Mar. 6. Azo dyes giving golden yellow tints on wool are formed from 1-(2'-methyl-3'-sulfo-5'-isopropyl)-phenyl-3-methyl-5-pyrazolone with aromatic diazo compds. such as those from aniline or similar compds.

**Dyeing.** AKT.-GES. FÜR ANILIN-FABRIKATION. Brit. 189,046, March 17, 1922. Furs, hairs, etc., are dyed with an aq. soln. contg. 4-aminophenol, or a substitution product thereof having the substituent in the nucleus, an alkyl ether of a diaminophenol and an oxidizing agent, with or without mordants. *E. g.*, a mixt. of 4-aminophenol hydrochloride, 2,4-diaminoanisole,  $\text{NH}_3$ , and  $\text{H}_2\text{O}_2$  produces on unmordanted fur a bordeaux dyeing and with Cu, Fe, and Fe mordants deep reddish tints. If 2-chloro-4-aminophenol be used in place of 4-aminophenol, violet to black dyeings are obtained, and a mixt. of 2,6-dichloro-4-aminophenol and 2,4-diaminoanisole or 2,4-diaminophenetole gives blue-black shades. The dyeing agents may be used either in the form of bases or their salts.

**Dyeing.** AKT.-GES. FÜR ANILIN-FABRIKATION. Brit. 189,054, April 18, 1922. Furs, skins, hairs, feathers, etc., are dyed in a soln. of a halogen- or nitro-deriv. of 4-amino-1-hydroxybenzene in the presence of an oxidizing agent with or without mordants. *E. g.*, the well washed skin is dyed in a bath contg. 2-chloro-4-amino-1-hydroxybenzene,  $\text{NH}_3$  and  $\text{H}_2\text{O}_2$ , brown tints being obtained. Brown shades are obtained with Cr or Cu mordants, while with Fe mordants the tints are reddish brown. 2,6-Dichloro-4-amino-1-hydroxybenzene gives greenish grey tints and 2-nitro-4-amino-1-hydroxybenzene reddish brown shades with Cr or Cu mordants.

**Dyeing wool.** AKT.-GES. FÜR ANILIN-FABRIKATION. Brit. 188,632, Apr. 13, 1922. The deterioration of wool caused by Cr compds. in dyeing with chrome dye-stuffs is prevented by the addn. to the dyebath, or to the after-treatment bath contg. the Cr compd., of sulfite-cellulose waste liquor or the constituents thereof such as ligninsulfonates, cell-pitch or sugars, particularly pentoses or hexoses. According to examples wool is dyed in a bath contg. sulfite cellulose waste liquor, the mordant and anthracene chromate blue XR, metachrome brown B or fast chrome brown 2R, in the last the dichromate being added after a preliminary boiling.

**Dyeing or coloring wood.** J. T. BOUWMAN. U. S. 1,447,528, Mar. 6. Wood or other fibrous material is colored throughout its entire mass by drying and immersing it in a dye soln. under pressure, employing a basic dye together with an excess of an acid dye, which produces a uniform coloration.

**Bleaching.** DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT FORM. ROESSLER AND A. SCHAIDHAUF. Brit. 188,811, Aug. 24, 1921. In bleaching straw, wool, cotton, and other textile fibers with solns. of  $\text{Na}_2\text{O}_2$  or strongly alk. solns. of  $\text{H}_2\text{O}_2$ , the bleaching lyes are arranged to come into contact, in the app. used, with surfaces only of pure Ni. Thus, metal pumps coated with Ni at the parts contacting with the lyes, Ni

tubes for the heating coils conveying the liquid, and Ni-plated Fe receptacles may be used; or the whole app. may be made of Ni.

**Embossing.** H. FUNASAKA. Brit. 188,562, Dec. 12, 1921. Cloth made from animal fiber is treated with a soln. of a sulfo cyanate prior to embossing it under heat and pressure. When the cloth so treated is pressed with a heated embossing calender, the fiber of the cloth curls and a permanent embossed design is obtained. KCNS is preferably used and a sheet of cotton cloth or waterproofed paper is preferably interposed between the cloth and the calender to prevent corrosion of the latter.

**Artificial silk; viscose and other cellulose solutions.** NAAMLooZE VENNOOTSCHAP NEDERLANDSCHE KUNSTZIJDE-FABRIEK. Brit. 189,114, Nov. 8, 1922. For purifying viscose, etc., solns. to be used in the manuf. of artificial silk, the soln. is emulsified with an org. liquid such as paraffin, which does not dissolve in the soln.; on standing the emulsion seps. into layers, and the org. liquid carries with it the suspended particles and a portion of the resinous and coloring impurities of the viscose, etc., soln. Sepn. may be accelerated by passing the emulsion through a centrifugal separator. Subsequent filtration is unnecessary. Cf. C. A. 17, 1142.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

**Microscopic measurements of pigment particles.** G. ST. J. PERROTT AND S. P. KINNEY. *Paint, Oil and Chem. Rev.* 75, No. 11, 10-11(1923). E. H.

**The testing of varnishes and paints especially the testing for durability to weather.** HANS WOLFF. *Farben-Ztg.* 28, 704-5(1923).—A glass jar fitted with cooling and heating coils, and in which humidity conditions can be varied, was used to study the effect of these variables on paint and varnish films. A report of the detailed study is not yet ready, but it is evident that the effects of light and variations in temp. are not nearly as severe as those of humidity, especially when there is dew and fog formation and a subsequent drop in temp. below the f. p. Humidity conditions during application and drying of the films may have tremendous influence on durability. F. A. WERTZ

**Production of driers from copals.** ANDÉS. *Farben-Ztg.* 28, 782(1923).—Resinate driers cannot be successfully made out of copal resins instead of rosin. Kauri, Congo, damar, and spirit-sol. manila copals were used in attempts to make fused and pptd. resinsates of Pb, Mn, and Co. When the resinsates could be produced at all, they were found to be insol. in linseed oil, turpentine, and mineral spirits, the only exception being the pptd. Mn resinate obtained from saponifying a heavily "run" Congo, and ppts. with  $MnCl_2$ . This drier gave fairly satisfactory results but its cost is prohibitive. F. A. WERTZ

**The preservation of iron and steel by means of paint.** J. N. FRIEND. *J. Oil Colour Chem. Assoc.* 5, 263-307(1922).—Presidential address. A historical review of the corrosion of Fe and its prevention by painting, is given, together with further results on previously started expts. (C. A. 13, 1156). Tung oil, and polymerized linseed oil produce less permeable films than raw linseed oil, and the use of the former in paints applied to steel plates gave increased protection. The effects of light, and the color of the paint upon time of drying and durability are discussed. Dark colored paints showed far greater protection against corrosion than light colored ones. Indian-red-linseed oil paints, contg. 60% pigment by wt., gave better protection than the same paint with a higher or lower pigment content; with red lead, max. efficiency was obtained with 80% pigment. Different pigments possess different optimum concns.; these appear to coincide generally with good brushing consistency. That two thin coats of paint give better protection than one coat of the same total thickness was

confirmed. The results obtained by varying the pigment content of paints used in multiple coat work indicate that a high % of oil in the priming coat, with a normal % of oil in the second coat, gave the best protection; but discussion brings out that this is contrary to American experience that a primer of high pigment content is desirable. Closely adherent scale should not be removed from iron and steel before painting. Illus. with plots and photos.

F. A. WERTZ

**Tube water colors.** HANS WAGNER. *Farben.-Ztg.* **28**, 779-81(1923).—A review of the compn. and properties of aquarelle and tempera colors, especially of the desirable properties imparted to the colors by the colloidal action of slight variations in the compn. of the vehicles. Different pigments require sp. proportions of gum arabic in the vehicle to produce pastes that will not gelatinize, will not sep. on addn. of  $H_2O$ , nor produce streaky films on application, etc. The quantities of gum required for various pigments are tabulated. This quantity is dependent on the sp. gr. and degree of dispersion of the pigment. Products such as glycerol, glycol, and especially oxgall, act as protective colloids thereby reducing the quantity of gum required, and improving the keeping qualities of the pastes in the tubes.

F. A. WERTZ

**Siccatives in various forms.** FRITZ ZIMMER. *Farben.-Ztg.* **28**, 705-6(1923).—Review.

F. A. WERTZ

**The heat treatment of China wood and linseed oils.** C. F. MABERY. *Ind. Eng. Chem.* **15**, 365-7(1923).—The I nos. of tung and linseed oils heated for various lengths of time at temps. up to  $200^\circ$  in air, in  $CO_2$ , and in closed vessels, indicate that the fatty acids in these oils polymerize to the condition of satn. of oleic acid. Mol. wts., ultimate analyses, I nos., and  $n$  of the heated oils and of their isolated fatty acids are tabulated.

F. A. WERTZ

**Relationship between resinification and the constitution of chemical compounds.**  
**III. A new process for preparing synthetic resins.** WALTHER HERZOG AND J. KREIDL. *Z. angew. Chem.* **35**, 641-3(1922); cf. *C. A.* **17**, 1339.—A new process of prep. synthetic resins consists in heating diarylolefin ketones of the type  $R[(CH=CH)_n - \dots - CO - \dots - (CH=CH)_n]R'$ . The resinophore group is  $-CO-CH=CH-$ . Resin from benzylidenacetone prep. by heating for 12 hrs. at  $230-40^\circ$  in  $CO_2$  is a red-brown, fairly hard product, m.  $60-5^\circ$ , sol. in most org. solvents. Resin from anisylidenacetone, prep. at  $220-5^\circ$ , and purified by repeated pptn. by dropping the  $Me_2O$  soln. into a large excess of petrol ether, is a yellow-white, amorphous powder, m.  $110-20^\circ$ . The formula is probably  $(C_{11}H_{15}O_2)_x$ . Resin prep. from cinnamylidenacetone, m.  $130-50^\circ$ , from cinnamylidenacetophenone, m.  $25-64^\circ$ , from *p*-di- $[\gamma$ -keto- $\alpha$ -butenyl]benzene,  $C_6H_4(CH:CHCOMe)_2$ , m.  $129-33^\circ$  (contains two resinophores); also from benzylidene, and cinnamylidene- $\alpha$ -tetralones,  $C_6H_4.CH_2.C(CH_2)(CH:CHR).CO$ .

J. B. BROWN

ANDRÉS, LOUIS EDGAR: **Praktisches Handbuch für Anstreicher und Lackierer.** 5th revised ed. Vienna & Leipzig: A. Hartleben. 287 pp.

ANDRÉS, ERWIN: **Die Fabrikation der Lacke, Firnisse, Buchdrucker-Firnisse und des Siegellackes.** 7th revised ed. Vienna and Leipzig: A. Hartleben. 280 pp.

ELLIS, CARLETON: **Synthetic Resins and Their Plastics.** New York: The Chemical Catalog Co., Inc. 500 pp. \$6.

SEHLIGMAN, FRANZ AND ZIEKE, EMIL: **Handbuch der Lack und Firnis-Industrie.** 3rd. ed. Berlin: Union Deutsche Verlagsgesellschaft. Reviewed in *Farben.-Ztg.* **28**, 706-7(1923).

WOLFF, HANS AND SCHLICK, W.: **Paint: Farben und Lackkalender Taschenbuch.** Stuttgart: Wissenschaftliche Verlagsgesellschaft. 177 and 149 pp.

**Paint.** W. H. ROBINSON. U. S. 1,445,173, Feb. 13. A paint for use on canvas awnings or curtains is formed of wheat flour 1 lb., oil paint 3.5 lbs., melted laundry soap 8 oz. and dried 0.5 pint.

**Paint.** KOMAKICHI KATO and IKUJI KAWAI. Japan. 40,312, Oct. 18, 1921. Soy bean (450 g.) is softened by immersing in  $H_2O$  for 12 hrs.; it is then crushed to a paste, dild. to 6 l. with  $H_2O$ , and agitated with  $NH_4OH$  (100 g.). After a few hrs. the mixt. is neutralized with a mineral acid and mixed with *Hydrosme rivieri* powder (60 g.). After 5–10 hrs., it is mixed with Ca caseinate, prepd. from casein (100 g.) and  $Ca(OH)_2$  (1.5–2.5 g.). For use the mist. is dild. with  $H_2O$  and mixed with suitable materials.

**Roof paint.** J. GOWER and H. WOLFE. U. S. 1,447,208, Mar. 6. Coal tar 1.5, melted rubber compd. 1.5 and varnish 1 part.

**Black carbonaceous pigment.** V. H. SCHNEE. U. S. 1,446,933, Feb. 27. CO is decomposed at 300–800° under pressure with Co as a catalyst.

**White lead.** C. P. TOLMAN. U. S. 1,447,740, Mar. 6. Pulverized metallic Pb is advanced continuously through a rotating horizontal inclined tubular chamber wherein it is treated with corroding reagents. The partially corroded Pb discharged from the chamber is "threshed" and passed through another chamber wherein the corroding treatment is continued to produce white lead.

**Oxygenated compounds of titanium and pigments containing said compounds.** G. CARTERET and M. DEVAUX. Can. 228,641, Feb. 13, 1923. Gelatinous  $TiO_2$  is dissolved in  $H_2SO_4$  and treated with H to ppt. the oxide which is freed from the soln. and calcined. The  $H_2SO_4$  may be neutralized with an alk. earth sulfate and the product washed with milk of lime completely to neutralize the acid.

**Lithopone.** F. G. BREYER and C. W. FARBER. U. S. 1,446,637, Feb. 27. Crude lithopone is pptd. in the presence of such an excess of BaS that after appropriate muffling for the production of a final product which is practically non-reactive to ultra-violet light, a product is obtained which (with methyl orange as indicator) requires 2–1 cc. 0.02 N  $H_2SO_4$  for titration to a faint pink color of 100 cc. clear filtrate obtained from a mixt. of 50 g. of the product with 250 cc. distd.  $H_2O$ , agitated for 5 min. at a temp. of about 20°. Lithopone prepd. in this manner mixes readily with paint oils.

**Lithopone.** W. R. MACKLIND. U. S. 1,447,592, Mar. 6. An app. is employed in which the lithopone is kept moving in a continuous operation from the time it is pptd. until it is packed after washing and settling.

**Lithopone.** J. A. SINGMASTER and F. G. BREYER. Can. 228,582, Feb. 6, 1923. Lithopone is subjected in a progressively operated vertical retort to a temp. of 550 to 800° in an atm. composed exclusively of the gases driven off from the lithopone by the muffling treatment.

**Lithopone.** P. R. CROLL and F. G. BREYER. Can. 228,580, Feb. 6, 1923. A soln. of BaS is mixed with a soln. of  $ZnSO_4$  of about 20° Bé. and having a Cl content, not in excess of 2 g. per liter and the resultant ppt. is muffled at 700 to 800°.

**Apparatus for manufacturing lithopone.** J. A. SINGMASTER and F. G. BREYER. Can. 228,581, Feb. 6, 1923. The app. comprises a vertically disposed and externally heated cylindrical retort of good heat-conducting material having a diam. of approx. 12 in. and a length of at least 25 ft.

**Rotary muffle furnace or kiln adapted for treating lithopone.** W. R. MACKLIND. U. S. 1,447,593, Mar. 6.

**Chinese ink.** BAISEN SUZUKI. Japan. 40,208, Oct. 5, 1921. Ink is prepd. by mixing C black 100, casein 60, thymol 1, boiled oil 5, soap 20, sugar 30,  $H_2O$  300 and a small quantity of perfumes. The casein is dissolved in  $NH_4OH$  or borax soln.

**Rotogravure ink.** A. SCHWENTERLEY. U. S. 1,447,734, Mar. 6. A mixt. of gasoline or a similar petroleum product with about  $1/3$  its vol. of  $CCl_4$  is used as a solvent for inks, together with usual pigments.



**Drying lithographed metal plates.** T. L. TALIAFERRO. U. S. 1,446,947, Feb. 27. Lithographed plates are carried on a conveyor through a drying oven heated to such a high temp. that oxidation and discoloration of the pigments would occur if the heating were sufficiently prolonged, while air is kept in motion in the oven and the operation is restricted in time to avoid damage.

**Varnishes; polishes.** A. SCHMIDT. Brit. 189,104, Oct. 16, 1922. Chlorinated montan or other mineral wax is used as an ingredient of varnishes and polishes. It may be used alone in soln. or mixed with oils, pigments, other waxes, and resins.

**Polishing composition.** J. RIGNEY. U. S. 1,445,557, Feb. 13. A polish for wood or metal surfaces is formed of spar varnish  $\frac{1}{2}$  pint, floor varnish 1 pint, Japan drier  $\frac{1}{2}$  pint, methyl salicylate 1 oz. and gasoline 3 qts.

**Controlling fumes from varnish kettles, etc.** R. S. PERRY and P. W. WEBSTER. U. S. 1,446,480, Feb. 27. An inert gas, *e. g.*,  $\text{CO}_2$ , is introduced (through perforated pipes) adjacent the inner surface of the kettle in which varnish ingredients or similar materials are being heated with evolution of fumes, at a temp. above that of the walls of the receptacle but below the temp. of condensation of the fumes. The fumes and gas are removed while maintaining a blanket of gas between the fumes and walls of the receptacle which serves to avoid secondary decompn. of the fumes.

**Oxidizable oil.** P. W. WEBSTER. U. S. 1,447,954, Mar. 6. A distillate of an air-drying fatty oil which is semi-solid at temps. below  $0^\circ$  and condenses below  $24^\circ$ , adapted for use in *ore flotation sepn.*, is prepd., *e. g.*, by recovery of fumes from varnish kettles.

**Synthetic resins from furfural.** M. PHILLIPS and G. H. MAINS. U. S. 1,441,598, Jan. 9. Resinous products are formed by reaction between furfural and *m*-nitroaniline,  $\alpha$ -naphthylamine, *p*-toluidine,  $\beta$ -naphthylamine, *m*-tolylenediamine, methyl ethyl ketone, *o*-toluidine, cymidine or xylidine. The formation of the resins from *o*-toluidine, cymidine and xylidine requires heating under pressure and use of HCl or other catalyst, and the use of pressure and an acid or alk. catalyst shortens the time of heating and lowers the temp. required generally for the production of the resins.  $\beta$ -Naphthylamine forms a resin at room temp. without a catalyst but usually temps. of  $150$ – $200^\circ$  are used for a period of 1–3 hrs. The resins are generally insol. in  $\text{H}_2\text{O}$ , somewhat sol. in turpentine, sol. in  $\text{C}_6\text{H}_6$ , acetone and furfural and the latter solns. form varnish stains suitable for use on wood. The resins, with oils, form good baking enamels. Any person in the U. S. may make use of the invention without payment of royalty.

**Resins from phenols and formaldehyde.** A. HEINEMANN. U. S. 1,441,981, Jan. 9. Na glycerate or other alkali metal glycerate 1–2% is added in pulverulent state to phenol-formaldehyde condensation products after complete elimination of  $\text{H}_2\text{O}$  in order to stabilize the color of the compn. and render it tougher and more flexible when used as a varnish. Larger amts. of the glycerate gradually induce an insol. condition of the resin although it can still be melted.

**Lac resin.** BHOPAL PRODUCE TRUST, LTD. Brit. 188,296, Oct. 29, 1921. Lac resin is sepd. from impurities such as woody matter, dye, sand, and bodies of the lac insect, by grinding the impure resin, with or without  $\text{H}_2\text{O}$ , to pass through a sieve having 40 holes to the linear in. and passing the finely ground product as a cream or pulp through a centrifugal separator.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERUBEL

**Electrometric determination of the acid value of fatty acids and fats.** R. KREMANN AND F. SCHÖPFER. *Seife* 7, 612–14, 656–9(1922); cf. C. A. 16, 3005.—The electrometric titration of fats and fatty acids in alc. soln. is possible, but in the case of palmitic acid the titration curve is not of a form agreeing with theoretical considerations, and

in the titration of caprylic and capric acids it is impossible to obtain a titration curve owing to the contamination of the Pt electrode surfaces with pptd. soap. Mech. cleaning of the electrodes appears to be impossible owing to the damage to the platinized surfaces caused thereby. The platinized H electrodes were therefore replaced by smooth ones, which were arranged half in air and half in the liquid to be titrated, and by this means it was possible to titrate fatty acids. The liquid was titrated with 0.1 *N* alc. alkali at room temp. The results were as satisfactory as those obtained with phenolphthalein as indicator or by cond. measurements, and the method has a greater range of application than the latter method. The use of 0.1 *N* aq. solns. for the electrometric titration is preferable to that of alc. solns. in special cases, such as that of sunflower seed oil, and is useful as a secondary method in cases where with the use of alc. solns. the bend in the potential-vol. curve is not sufficiently well marked. Titrations with 0.5 *N* aq. solns. are not to be recommended in consequence of the more marked disturbance due to the sepn. of soap, which interferes with the equil. of the soln. The chief condition for obtaining satisfactory potential curves is to wait for a steady potential to be reached after each addn. of alkali. Disturbances due to the sepn. of soap on the electrode can be overcome by scraping the smooth electrodes. J. S. C. I.

**Naphthalenesulfonic acids as agents for hydrolyzing fats.** F. ТРЕПКА. *Przemysl Chem.* 6, 49-56 (1922).—The  $\alpha$ - and  $\beta$ -naphthalenesulfonic acids and 1,5-, 2,7-, 1,6-, and 2,8-naphthalenedisulfonic acids were tried as fat-hydrolyzing agents. The position and no. of sulfonic groups have no influence on the course of the reaction and the presence of these naphthalenesulfonic acids does not accelerate the hydrolysis of fats unless other compds. are present, which form complexes with the sulfonic acids. For instance the presence of Turkey-red oil considerably increases their fat-hydrolyzing properties. J. S. C. I.

**Fat-hydrolyzing catalysts.** A. E. SANDELIN. *Ann. acad. sci. Fennicae* [A] 19, 13 pp. (1922).—The reagents prepd. from petroleum (Happach) and naphtha contain no carboxyl groups. All these reagents have the following properties in common. They are of high mol. wt., are sulfonic acids, easily sol. in water and can be pptd. by the addn. of acids or NaCl; they are easily sol. in alc. and slightly sol. in ether. Their aq. solns. foam strongly, as also do solutions of their alkali salts, which are sol. in alc. Their alk.-earth and metallic salts are amorphous and insol. in water, but are often sol. in alc. Their action in the hydrolysis of fats is due first to their action as emulsifier of fat with water and secondly to the fact that they are strong acids and as such accelerate the hydrolysis. Their action is intensified by the addn. of  $H_2SO_4$ . Many sulfonic acids of high mol. wt. have been prepd., such as those from oleic acid with toluene, cymene, terpenes, alcs., and benzene, thymol, or naphthalene, and their fat-hydrolyzing action has been tested. All had considerable effect as fat-hydrolyzers, with the exception of those prepd. from oleic acid and toluene or cymene. The failure of those is no doubt due to the decompn. of the sulfonic acids by boiling water. J. S. C. I.

**Constitution of Twitchell's reagent.** A. E. SANDELIN. *Ann. acad. sci. Fennicae* [A] 19, 19 pp. (1922).—Hydroxystearic acid, hydroxystearosulfuric acid, and  $\alpha$ - and  $\beta$ -naphthalenesulfonic acids possess no fat-hydrolyzing properties, but a compd. with feeble fat-hydrolyzing properties is obtained when a mixt. of hydroxystearosulfuric acid or hydroxystearic acid and  $\alpha$ -naphthalenesulfonic acid is treated with  $H_2SO_4$ . By oxidizing Twitchell's reagent with alk.  $KMnO_4$ , an acid was obtained the lead salt of which had the empirical formula,  $C_{18}H_{24}O_{11}Pb$ . Analysis indicated a tricarboxybenzene. The free acid consisted of prisms m. 189-90°, sol. in ether, alc., and acetone, but only slightly sol. in light petroleum spirit,  $CCl_4$ , and  $CHCl_3$ . The Na and K salts are easily sol., the Ba salt slightly sol. in water. The Ag salt is sol. in hot water. Analysis of the free acid gave the formula  $C_{18}H_{24}O_{11}$ , and it is in all probability hemimellitic acid.

The difficultly sol. Ba salt of another acid, benzene-1,2-dicarboxy-4-sulfonic acid, was also isolated. The formation of these two acids leads to the conclusion that Twitchell's reagent is formed by combination of the naphthalene with the double bond of the oleic acid and sulfonation of the addn. product, and that it has the constitution  $C_{10}H_8O_2C_2O_4H_2SO_4$ . In all probability fat-hydrolyzing agents prepd. from naphthalene and ricinoleic acid, castor oil or their hydrogenation products are of analogous constitution. The "Kontakt" fat-hydrolyzer is, on the other hand, of different constitution, for here the sulfonic acid of high mol. wt. contains no carboxyl groups. J. S. C. I.

**Determination of volatility of oils.** A. R. MATTHIS. *Bull. Fed. Ind. Chim. Belg.* 1, 397-405(1922).—Some precautions that should be taken in measuring the evapn. of oils on being heated are frequently omitted and thus contradictory results are obtained. In addn. to the quantity of oil used for the test and the temp. and duration of heating, the area of exposed surface and the projection of the vessel above the surface of the oil should be taken into account as these have a definite bearing on the rate of evapn. M., using vessels of different shape and different quantities of oil, shows that in extreme cases loss of wt. may vary by 228% under otherwise identical conditions of heating. Details of a no. of expts. are given and suggestions for the standardization of the tests are put forward. J. S. C. I.

Some useful matters contained in the forest trees in Japan. I. Fatty oil contents in seeds of various forest trees in Japan. HACHIRO MIURA. *J. Chem. Ind. (Japan)* 25, 1277-305(1922).—Crude fat contents in seeds and endosperm of 44 species of Japanese forest trees are given. The weighed seeds were dried and examd. under the microscopes. Those contg. the fatty oil were selected and ground with and without their coats. The samples were then dehydrated with anhyd.  $CuSO_4$ , pulverized, mixed with  $Na_2SO_4$ , and extd. with  $Et_2O$  for 3 hrs. in a Soxhlet app. The loss of wt. by 15 g. of the sample by heating at  $100^\circ$  for 4 hrs. was calcd. as  $H_2O$ . The characteristic of the fatty oils obtained by pressing the seeds which have a particularly high fat content are given, resp., for *Sciadopitys verticillata*, S and Z; *Magnolia grandiflora*, L; *Magnolia kobus*, DC; *Magnolia abovata*, Thumb; *Xanthoxylum piperitum*, DC; *Fagara schinifolia*, Engl; *Phellodendron amureuse*, Rupr; *Tilia cordata*, Mi (var. *japonica*, Miq.) as follows:  $d_{15}$  0.9407, 0.9245, 0.9337, 0.9305, 0.9409, 0.9441, 0.9447, 0.9430; acid value 3.2, 12.2, 21.0, 11.3, 1.77, 29.9, 2.4, 3.6; sapon. no. 187.5, 186.8, 188.9, 190.5, 193.0, 187.7, 188.7, 185.5; Wijs. no. 162.8, 117.2, 118.9, 133.7, 132.6, 144.1, 122.2, 120.5; ester value 184.3, 174.6, 167.9, 179.2, 175.3, 157.8, 186.3, 181.9;  $n_{20}$  1.4810, 1.4756, 1.4741, 1.4777, 1.4778, 1.4775, 1.4856, 1.4766; R.-M. value 4.9, 1.0, 1.3, 0.9, 2.6, 2.2, 3.2, 1.4; acetyl value 32.8; 24.0, 20.5, 12.4, 22.1, 42.0, . . . , 27.4; and unsapon. matter in % 3.84, 2.14, 2.90, 1.71, 3.19, 0.51, 2.50, 1.53.  $H_2O$  content, % of oil yield and description of the seed and trees are given for each of 44 species. S. T.

**Properties of walnut oil.** KAZUO MATSUMOTO AND YOSHISUKE UYEDA. *J. Chem. Ind. (Japan)* 25, 1438-40(1922).—The characteristics of walnut oil obtained from *Juglans Sieboldiana* from Ishikawa were detd. The kernel contains 4.99%  $H_2O$ , and 59.58% oil, the latter having a light yellow color and pleasant odor. Its  $d_{15}$  is 0.9332,  $n_{20}$  1.4800, acid no. 0.68, Hehner value 92.3, sapon. no. 191.1, R.-M. value 0.62, Hübl's no. 150.8. It does not solidify at  $-16^\circ$ . The surface layer of the oil dries at  $100^\circ$ . It, therefore, belongs to the drying oils. S. T.

**Modern edible-oil manufacture by extraction with subsequent refining.** E. W. ALBRECHT. *Seifenleder Ztg.* 50, 65(1923).—It is a regular practice in modern plants to ext. down to 1% and even 0.65% oil content in the pressed goods, but it is uneconomic to go as low as 0.1%, on account of the long time required. Soy-bean press cakes alone have been proposed as human food. Unrefined extd. oils have not necessarily a bad odor, nor are they dangerous to health. A. has produced sunflower oil for human

consumption without previous refining. The modern extn. plant is reliable, requires no after-drying of extd. goods, needs no mechanical agitators and has grate bottoms that require no filter cloths.

P. ESCHER

**Short laboratory notes.** J. GROSSER. *Seifensieder Ztg.* 50, 37(1923).—In recovering alc. from soap solns., the latter must first be made alk. otherwise volatile esters, from coconut-oil soaps, will pass over, influencing the sapon. no. in future detns. In Twitchell control work the fatty acids should not be heated before diln. with alc., else fatty anhydrides will form and diminish the acid no. and increase the ester no.

P. ESCHER

**Modern wool-fat plants.** F. WOLFF. *Chem.-Ztg.* 47, 59-60(1923).—The wool wash waters, instead of being acidified, are evapd. and the wool fat is removed by extn. with benzine. This process has the advantage of recovering the soap used in washing and is cheaper.

E. SCHERUBEL

**A chemical study of the liturgical waxes.** EDUARDO VITORIA. *Mem. acad. cienc. artes, Barcelona* 17, 185-229(1921).—This paper deals with the detn. of the phys. consts. and chem. compn. of the com. waxes used in the Catholic Church ceremonies and masses.

GEORGE W. PUCHER

**Synthesis of fats (AMBERGER, BROMIG) 10.** **Manufacture of hydrocarbon oil from fatty oils or acids (Japan. pat. 40,210) 22.**

THALMANN, FRIEDRICH: *Die Fette, Oele und Wachsarten. Ihre Gewinnung und Eigenschaften.* 4th Ed. revised. Vienna and Leipzig: A. Hartleben. 392 pp. M 150.

**Neutralizing fatty oils.** H. SCHLOSSSTEIN. U. S. 1,447,898, Mar. 6. Coconut oil or other fatty oils are mixed with glycerol to combine with free fatty acids under pressure together with sulfo-fatty acids and a common solvent, e. g., acetone or alc. and the mixt. is emulsified, mixed with another quantity of the material contg. fatty acids *in vacuo* and H<sub>2</sub>O is evapd. The temp. of the material delivered to the emulsifier is reduced in order to lower the emulsifying temp.

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

**Note on the raw sugar of the last campaign.** G. SCHECKER. *Z. Ver. deut. Zuckerind.* 73, 109(1923).—The sugars were unusually alk., the affination sirup showing an alk. of 0.05%.

F. W. Z.

**The affination of raw sugar.** G. SCHECKER. *Z. Ver. deut. Zuckerind.* 73, 108-12(1923).—The yield of affined sugar and the purity of the sirup obtained depend not only on the grain of the raw sugar, but also on the degree of satn. of the sirup used for affining. This sirup is often far from satd., because it is heated by means of a steam jet. A closed coil would be preferable. A table is given which shows the Brix that a sirup of different degrees of purity must have to be satd. for varying temps. of the magma. The table shows that the Brix of the satd. sirup decreases with an increase in the purity. The molasses surrounding the sugar crystals was found to be exhausted, and it has therefore no effect on the supersatn. ratio of the satd. sirup. As long as a refinery is operated under the same conditions, there is generally an equil. between the Brix and the purity of the sirup used for affining. If the run-offs and washings from the centrifugals are not sepd., the yield of affined sugar can be calcd. from the non-sugar and polarization of the raw sugar and the purity of the affination sirup. F. W. Z.

**Density determinations.** C. BRENDL. *Z. Ver. deut. Zuckerind.* **73**, 27-61 (1923).—The fundamental definitions and units of mass, vol., d., sp. gr., and the different app., methods and tables used in detg. the concn. of sugar solns. are critically analyzed, and many common errors and misconceptions are pointed out and corrected.

F. W. ZERBAN

**Detection of sugar in condensed waters by means of cresol.** G. E. STEVENS. *Ind. Eng. Chem.* **15**, 363(1923).—Dissolve 6 g. Castile soap in 100 cc. water and mix with 15 cc. cresol. Warm and agitate, and add more soap if necessary. Pour the condensed water to be examd. into a test tube of 15-25 mm. diam. to the height of 1 in., add 5-10 drops cresol reagent, mix thoroughly, cool, and run concd.  $H_2SO_4$  below the aq. layer to a height of 0.5 to 0.75 in. Roll the tube gently. One % sugar gives a reddish black ring turning black, and in a dilm. of 0.0001% a light pink develops in 1-2 hrs. A table is given showing approx. concns. of sugar corresponding to appearance of the ring. Traces of oil, iron, lime salts, ammonia and other mineral salts do not interfere as they do in the  $\alpha$ -naphthol test.

F. W. ZERBAN

**Statistics of the distribution and yield of cane varieties in the season of 1921.** J. VAN HARRVELD. *Arch. Suikerind.* **30**, Mededeel. *Proefstation Java-Suikerind.* 533-612(1922); cf. *C. A.* **15**, 1417.—Complete data are given for 172 out of 183 factories. The principal varieties in the order of area planted are EK 28 (38.75%), 247 B (21.25%), DI 52 (14.75%), and 100 POJ (6.25%).

F. W. ZERBAN

**The Thomas and Petree process in Hawaii.** S. S. PECK. *Intern. Sugar J.* **25**, 26-33(1923).—The Thomas and Petree process is described, and its advantages enumerated. It is estimated that the saving from the process in a factory producing 25,000 tons of sugar would amount to \$41,478. After deducting interest charges on the investment, and loss of filter press cake, the saving resulting from the process is estimated at \$23,428, or 39% on the investment.

W. L. OWEN

**Mill setting.** G. J. VAN HAM. *Arch. Suikerind.* **31**, 72-81(1923).—One of the principal factors detg. extn. and fuel value of the bagasse is the opening between the different rollers. Proper relations between openings for front and back rollers are given, for different varieties of cane, based on practical experience. The working and operation of hydraulics are discussed, and other practical advice is given.

F. W. Z.

**Conveying massecuites.** G. SCHECKER. *Z. Ver. deut. Zuckerind.* **73**, 112-5 (1923).—The massecuite must be highly concd. to give a good yield of crystals. If it becomes too stiff, it should not be dild. with water, but mixed with a satd. green sirup. To facilitate the transportation of stiff massecuites, the opening of the pan must be wide enough, 20-4 in. The mixers should be placed directly under the pans. To conduct massecuites interchangeably from several pans into several mixers, a tipping gutter may be used, or an intermediate trough, with or without conveyors, and provided with cut-off slides. If the centrifugals are not directly under the mixer, the massecuite must be pumped; this causes a fall in temp. and poor purging. Where the centrifugals are fed directly from the mixer, care must be taken that water added surreptitiously will not mix with the massecuite.

F. W. ZERBAN

**Extraction of sugar from beet molasses by a modification of the baryta process.** H. MANOURY. *Bull. assoc. chim. suc.* **39**, 413-21(1922).—BaS (obtained by the reduction of the sulfate by heating with charcoal to 1000-1200°) is treated with hot water, and the resulting liquor, after filtration, mixed with ZnO and heated, the soln. of Ba(OH)<sub>2</sub> thus obtained being used for the prepn. of Ba monosaccharate, which is filtered off in presses. In order to decompose this saccharate cake, it is heated with a soln. of ZnSO<sub>4</sub>, the soln. of pure sugar obtained being worked up as "refined." Regarding the by-products resulting from this method of operating, the ZnS is treated with H<sub>2</sub>SO<sub>4</sub> to produce the ZnSO<sub>4</sub> used for the decompn. of the saccharate cake; while the

mixt. of  $\text{BaSO}_4$  and  $\text{Zn(OH)}_2$  resulting from the decompn. of the saccharate cake is mixed with the wash-waters from the process of leaching out the  $\text{BaS}$ , the  $\text{Ba(OH)}_2$ , filtered off, and the residue (consisting of  $\text{ZnS}$  and  $\text{BaSO}_4$ ) treated with  $\text{H}_2\text{SO}_4$  for the recovery of more  $\text{ZnSO}_4$ . It is stated that this process is in routine operation in a sugar factory in Spain. J. S. C. I.

**Rate of decomposition of some nitrogenous constituents of beet juice by lime.** J. VONDRÁK. *Z. Zuckerind. Czechoslovak Rep.* 46, 483-90, 533-9, 589-97 (1922).—Lab. expts. carried out with aq. solns. of various amides in the presence of lime, under conditions resembling those prevailing in the factory during defecation, showed glutamine to be very readily decomposed, asparagine more slowly, and choline and allantoin only inappreciably. A more rapid decompn. of asparagine resulted when the lime was added in the cold and the soln. subsequently heated, than when the addn. was made at a high temp., and it is therefore suggested that in the factory defecation should be carried out in the cold. As a means of preventing the retrogression of the alkyl during evapn. and boiling, it is advisable that lime should be added in the second carbonatation, the satn. at this stage being carried out with  $\text{CO}_2$  at  $100^\circ$ . J. S. C. I.

**Liming raw beet juice and the separation of the resulting precipitate by subsiding.** V. SKOLA. *Z. Zuckerind. Czechoslovak Rep.* 46, 601-11, 625-9 (1922).—Expts. carried out with the object of effecting a preliminary sepn. of the albuminoids from beet juice by the addn. of lime and subsiding showed that the rate at which the ppt. settled out was not dependent solely on the amt. of lime, but largely upon the manner in which the addn. was made. Generally the best results in respect of rapidity of subsiding were obtained by running the diffusion juice into milk of lime while constantly stirring; under these conditions when 1%  $\text{CaO}$  was used about 0.2%  $\text{CaO}$  was retained in the sediment. A less favorable result was obtained when about 0.2%  $\text{CaO}$  in the form of milk of lime was added to the juice and the mixt. heated to about  $80^\circ$ . J. S. C. I.

**Action of lime on the protein substances separated during the defecation of beet juice.** V. STANEK. *Z. Zuckerind. Czechoslovak Rep.* 46, 663-9, 671-6 (1922).—Raw beet juice was limed and heated, and the effect of this treatment on the proteins thus pptd. was studied. It was found that under the conditions of liming in practice, about 11% of the ppt. may pass into soln., but part will be repptd. on carbonating. This hydrolytic action of lime was found to result in the formation of albumoses, peptones, and polypeptides, but it was not possible to isolate amino acids. Decompn. products of lecithin, e. g., glycerophosphoric acid and choline, were detected. Betaine could not be identified. J. S. C. I.

**Changes in composition of beet leaves and tops stored in the field.** K. WODARZ. *Z. Ver. deut. Zuckerind.* 73, 2-27 (1923).—Considerable losses are experienced when these materials are stored in silos. Expts. on the advisability of storing them in the field were therefore made, and the changes in compn. closely followed by complete analyses, the results of which are given in detail. Conclusions: Siloing should be used only as an emergency measure, and as little as possible. The losses in food value of beet leaves and tops left in the field up to the end of December are much smaller than if they are placed in silos. The fodder keeps best when spread in thin layers. The loss in food value is greater in the leaves than in the tops, and sep. storage may be advisable. The intentional wilting of the leaves is not justified by the facts.

F. W. ZERBAN

**A remarkable occurrence of urea.** E. O. VON LIPPMANN. *Ber.* 56, 566-7 (1923).—The blind end of a pipe connected with the steam exhaust of the boiler house of a beet-sugar factory was found to be filled with almost pure urea. The end of this part of the pipe had been screwed up and it had long been unused. Ammonium carbonate had previously been found deposited in steam exhaust pipes from beet-sugar factories and

it is suggested that the urea found in this case probably originated from ammonium carbamate. P. A. CAJORI

**Bone-char and decolorizing carbons.** G. AVOR. *Facts About Sugar* 16, 170 (1923).—A comparative study of the efficiency and cost of refining sugar by the two processes giving figures for revivification losses, cost limits, ash absorption, loss in sugar yield as well as a discussion of the added advantages of carbons. N. K.

**Experiments with various decolorizing carbons.** E. SAILLARD. *Suppl. Circ. Syndic. Sucre de France* 1922, Nos. 1724, 1726, 1728, 1730, 1734.—To 50-cc. portions of a 20% soln. of beet molasses. 0.5 g. of decolorizing C, or 0.5 g. of finely ground animal charcoal, was added, the temp. being maintained at 78–80° during 20 mins. After cooling, and filtering, the color removed, expressed as % of original color, was found to be as follows: animal charcoal 27, "Norit" 43, "Darco" 44, and "Carboraffin" 75. Practically the same results were obtained when the treatment was carried out at the ordinary temp. Other expts. led to the following conclusions: A better decolorization results when the treatment is effected under pressure at 110° than at 78–80°; the finer the state of division of the carbon the better its action in adsorbing color; animal charcoal adsorbs about twice the amt. of Ca salts from soln. in comparison with "Carboraffin," and 3 times that retained by "Darco." On the other hand, animal charcoal takes up less free alkali than "Darco." J. S. C. I.

**Researches on maize starch sirup (glucose).** E. PAROW. *Z. Spiritusind.* 45, 229(1922).—Chem. examn. reveals but little difference between sirups prepd. from maize starch and potato starch, but the latter are usually more satisfactory when subjected to the "confectioner's test" (*i. e.*, little or no discoloration on heating to 145°). Complete analyses of a no. of starches and sirups indicated that the discoloration on heating was influenced by the fat and protein contents of the sirups. The addn. of fat to a sirup increased the discoloration. A sirup with 0.06% fat and 0.09% protein showed little alteration on heating to 145°; but others having 0.14–0.19% fat and 0.19–0.39% protein were badly discolored. High fat content may frequently be avoided by limiting the amt. of oil added to prevent frothing in the vacuum app. during the manuf. of glucose. J. S. C. I.

**Photomicrographs of the more common starches.** C. B. FALL. *Chem. Age* (N. Y.) 31, 37–9(1923).—Photomicrographs of 11 kinds of starches are given. *Soy bean starch* was prepd. from pure meal by successive extn. with  $\text{CCl}_4$ ,  $\text{H}_2\text{O}$ , 10% NaCl soln., 0.2% HCl soln., and  $\text{C}_2\text{H}_5\text{OH}$ . WM. STERICKER

The injurious effect of even the smallest contamination of cement and concrete by sugar (HUNDESHAGEN) 20. Air humidity and drying (PARR) 13.

•CLAASSEN, H.: *Die Zucker-Fabrikation*. 5th Ed. Revised and enlarged. Magdeburg, Germany: Schallehn & Wollbrück. 20s. Reviewed in *Intern. Sugar J.* 25, 97(1923).

DRACHMAN, P. AND ESTRUP, L.: *Aktieselskabet de Danske Sukkerfabrikker, 1872–1922*. Copenhagen. Reviewed in *Arch. Suikerind.* 31, 84–9(1923).

SAILLARD, ÉMILE; *Betterave et sucrerie de betterave. Le controle chimique de la fabrication du sucre de betterave*. 3rd Ed. Paris: Baillière et fils. Fr. 10.

**Controlling hydrogen-ion concentration in use of decolorizing carbons.** J. F. BREWSTER AND W. G. RAINES, JR. U. S. 1,447,461, Mar. 6. Sufficient HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ , HOAc or other acid is added to decolorizing C, diatomaceous earth, fuller's earth or similar materials to give them a  $p_{\text{H}}$  of about 4 at the time they are treated with decolorizing C. After the treatment they are neutralized with alkali. Decolorization

at this pH serves to enhance the decolorizing effect on sugar solns. This pat. is assigned to the Government and people of the United States, for free use.

**Starch solutions.** A. REYCHLER. Brit. 188,992, Dec. 15, 1921. The starchy material is first digested for about 20 hrs. with a dil. acid soln. of  $K_2Cr_2O_7$  or  $KMnO_4$ , or with  $KMnO_4$  soln. alone, the excess oxidizing agent being then reduced, e. g., by addn. of  $H_2SO_4$ . The product is treated with boiling  $H_2O$  and the suspension clarified by addn. of an alk. substance to a concn. of about 0.01 N. The last two operations may be combined into one. Suitable alk. substances are caustic alkalies,  $NH_3$ ,  $Na_2CO_3$  and borax.

**Starch.** A. SINGER. Brit. 188,344, Nov. 6, 1922. Starch which swells in cold  $H_2O$  to a jelly-like transparent mass is obtained by grinding starch or starch-contg. materials with dry caustic alkalies. The mixt. may be further treated with the stoichiometrical quantity of a stable org. acid or acid salts to obtain a neutral product. E. g., 100 kg. of potato flour and 5-10 kg. of NaOH are ground together for several hrs. The product may be used directly, or neutralized by further grinding with 6-11 kg. of oxalic acid.

## 29—LEATHER AND GLUE

ALLEN ROGERS

**Report of the chrome commission.** U. J. THUAU. *Cuir* 12, 95-6(1923); *J. Soc. Leather Trades' Chem.* 7, 73-5(1923).—Review of recent work on chrome leather and liquor analysis and outline of suggested work. F. L. SEYMOUR-JONES

**Art and science of leather manufacture.** F. L. SEYMOUR-JONES. *Chem. Met. Eng.* 28, 200-5, 400-3(1923); cf. *C. A.* 17, 648.—General descriptive articles from a scientific standpoint, covering vegetable tanning materials, vegetable tanning, currying, theories of tanning; fat, smoke, and aluminium tanning and tawing; one- and two-bath chrome, HCHO, quinone, and combination tannages; chamois, patent, and fish leather manuf.; water supply, by-products, chrome and lime sores. F. L. S.-J.

**Cellulose acetate in the manufacture of artificial leather.** MAURICE DESCHENS. *Cuir* 12, 58-9(1923).—Review of patents and their application. F. L. S.-J.

**The acidity of leather.** JALADE. *Cuir* 12, 8-10(1923).—The leather is extd. with water.  $SO_2$  is estd. in the water-sol. material directly and after neutralization with NaOH. The extd. leather is air-dried and divided into two equal portions. The one is ashed and  $SO_2$  in the ash estd. The other is extd. with a 1% soln. of  $K_2CO_3$  or of  $K_2CO_3$  and  $KNO_3$ , the ext. evapd., incinerated and  $SO_2$  in the ext. estd. This method avoids the errors due to  $MgSO_4$ . With sulfited exts., most of the S compds. are found in a form insol. in water. The effect of syntans was not examd. F. L. S.-J.

**Fire and the leather industry.** FÉLICIEN MICHOTTE. *Cuir* 12, 83-5(1923).—Untanned leather burns only with difficulty in strong drafts. Tanned leather, especially that fat-liquored or stuffed with oils or fats, burns more readily, and the oxidation of these oils may lead to spontaneous combustion. Bark mills are dangerous from dust and should be placed outside the tannery proper. Lime must be kept in a damp-proof store. Dangerous operations include melting currying waxes over an open flame, sizing with solns. of  $CS_2$  and benzene, the use of coke stoves in drying chamois leather, the manuf. of varnishes and the drying of patent leather. F. L. S.-J.

**Histological examination of skin.** M. L. KRALL. *Cuir* 12, 60-5(1923); cf. *C. A.* 16, 2427.—In staining the chem. nature of the tissue and of the stain must be considered. The skin consists of carbohydrates, fats and proteins. The carbohydrates are small in quantity and chiefly in combination with the proteins. The fatty matter of the skin comprises neutral fats, lecithins, and cholesterol. Dimethylaminoazobenzene (yellow)



Sudan III (red), and Scarlet R (dark red) are sol. in fats and are used as stains. Unsattd. fats are stained with osmic acid. Free fatty acids and soaps are stained with Nile blue sulfate. Basic dyes, such as methylene blue, methyl green, and safranin, stain cell nuclei and bacteria, while acid dyes give a general diffuse color over the whole of the skin section. Collagen stains well with acid fuchsin; elastin with resorcinol, fuchsin or orcein; muscles and keratin with picric acid. Details for staining are given.

F. L. SEYMOUR-JONES

**The vital resistance of ravaging insects of skins, furs and wools.** ANTOINE RIGOT. *Halle aux cuirs* 1923, 1-10.—Maintenance of a vacuum of a few mm. followed by the introduction of illuminating gas, the use of naphthalene, camphor, pepper, tobacco, pyrethrum powder,  $\text{CO}_2$ ,  $\text{CCl}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{SO}_2$ , while in some cases temporarily asphyxiating the larvae, failed to kill them.  $\text{CS}_2$  used for a sufficient length of time proved efficacious in their destruction.

F. L. SEYMOUR-JONES

**Bacteriology of fresh steer hide.** G. D. McLAUGHLIN AND G. E. ROCKWELL. *J. Am. Leather Chem. Assoc.* 17, 325-40(1922).—The authors have isolated and studied a no. of bacteria from fresh hide. Expts. on pieces of hide show that the presence of proteolytic bacteria, protein matter such as blood, a slightly alk. medium, a moderately high temp., the presence of O and small traces of  $\text{CO}_2$  favor bacterial decomp. of the hide, while the absence of proteolytic bacteria, acidity, the presence of fermentable carbohydrates, a large excess of  $\text{CO}_2$ , the absence of O, and a low temp. tend to prevent it.

J. S. C. I.

**Colloid chemistry and tanning.** H. STIASNY. *Kolloid-Z.* 31, 299-301(1922).—Brief mention of some of the more salient points in the application of colloid chemistry to leather manuf.

J. A. WILSON

**The tanning industry at the colonial exhibition at Marseilles, 1922.** E. JALADE. *Cuir* 12, 78-82(1923).—Review of the resources in hides, skins, and tanning materials, and of indigenous methods of tanning of the French colonies.

F. L. S.-J.

**Preliminary study of the tanning process.** B. HENNIG AND A. LOTTERMOSER. *Kolloid-Z.* 32, 51-6(1923).—Results are given of expts. to det. the amt. of adsorption of NaOH, KOH, LiOH,  $\text{Na}_2\text{CO}_3$ , and  $\text{Na}_2\text{S}$  by hide powder. Formaldehyde-treated hide powder was found to adsorb more alkali than the untreated hide powder. LiOH is adsorbed to a greater extent than the other alkalies, and causes less swelling of the hide powder. The presence of  $\text{Na}_2\text{CO}_3$  in NaOH decreases the amt. of NaOH adsorbed. When a hide powder is treated with  $\text{Na}_2\text{CO}_3$  or  $\text{Na}_2\text{S}$  adsorption takes place owing to the fact that the NaOH formed by hydrolysis is taken up by the hide powder.

C. T. WHITE

**Tanning materials in the Far East.** LLOYD BALDERSTON. *J. Am. Leather Chem. Assoc.* 16, 367-74(1921).—Except for a few myrobalans, China produces no vegetable tanning materials and the tannages used are smoke and mineral; a few modern tanners employ the chrome process. In Japan two species of oak are principally used, *Quercus dentata* with 11% tannin and 10.5% non-tans in the bark and 7% of each in the wood, and *Q. grosseserrata*, with 9.2% of each in the bark and a quarter as much in the wood. The root of the beach rose, *Rosa rugosa*, contains 24% tannin (dry basis) and is used as a mordant. The bark of 25 and the wood of 8 species of trees were examd. The results for the more important are given in % tannin and non-tans resp. Willow (*Salix purpurea*), bark, 7.5, 23; chestnut (*Castanea pubinervis*), bark, 6, 7; wood, 7, 4; yew (*Taxus cuspidata*), bark, 9.5, 16; larch (*Larix dahurica*), bark, 8.5, 6; spruce (*Picea glehnii*), bark, 19.2, 12.4. Complete analyses of eleven materials are cited.

F. L. S.-J.

**Tannin analysis and the conference.** H. R. PROCTER. *J. Soc. Leather Trades' Chem.* 5; 219-22(1921).—Twelve yrs. experience of the European official method of

tannin analysis shows that it is of great value but requires investigation and review in details. Extn. of solid materials is generally satisfactory. More automatic extn. and a method of grinding with less loss of moisture are desirable. Temp. of extn. is important in detg. sol. and difficultly sol. tannins, part of the latter often being classed as insol. matter. Since tannins are probably entirely in colloidal soln., the temp. of filtration, and rate of cooling affect the size of particles. Filtration, whether by paper and kaolin or by a Berkefeld candle, is liable to give rise to discrepancies. The term "optically clear" is indefinite; transparent tannin solns. will show a decided Tyndall cone. The acidity of the tannin solns., which is not standardized, will affect the amt. of tannin taken up by hide powder. Thorough washing of the hide powder to remove non-tannins is of doubtful value, since some are parent substances of tannins and hence practically useful. A more scientific method of color measurement is also desirable.

F. L. SEYMOUR-JONES

Report of the second series of trials of the commission for the quantitative analysis of tanning materials of the French section of the Society of Leather Trades' Chemists. G. HUGONIN. *Cuir* 12, 32-6(1923); cf. *C. A.* 17, 349.—A method was outlined in minute detail on the general lines of the European official procedure, and samples of chestnut, solubilized and natural quebracho exts. were analyzed by six analysts. With one exception, satisfactorily concordant results were obtained for water and total solids. For sol. and insol. material, both with the Berkefeld filter candle and with S. and S. filter paper 590, agreement between analysts was poor. The candle filtration is preferred as more rapid. The importance of exactly following directions for each of the minute details is again emphasized. Further work will be done on the best  $pH$  for tannin fixation and on the amt. of hide powder necessary for detannization. F. L. S.-J.

Notes on tannin analysis and practical reflections arising therefrom. E. SCHELL. *Cuir* 12, 36-7; *J. Soc. Leather Trades' Chem.* 7, 69-71(1923).—Since in analysis the amt. of tannin is found by difference from three direct detns., the error to be expected will be from 0.5 to 1.0 unit of tannin. War experience proved that 0.5 unit was too low, while a 1.0 unit difference included all cases except those with obvious errors. A method embodying the direct detn. of tannin, such as the latest modification of the Wilson-Kern method (*C. A.* 15, 3766), deserves consideration. F. L. SEYMOUR-JONES

Further observations on the Wilson-Kern method of tannin analysis. G. W. SCHULTZ. *J. Am. Leather Chem. Assoc.* 16, 349-67(1921); cf. *C. A.* 15, 609; Wilson and Kern, *C. A.* 14, 2103.—The washings from the tanned hide powder were analyzed and found to contain tannin. Not all the tannin is removed from the washings by a first charge of hide powder, since repeated extn. with fresh hide powder removes further tannin, even though the soln. gives a negative gelatin-salt test. When 8 l. of detannized soln., giving a negative gelatin-salt test, are evapd. to 200 cc. then rediluted to 8 l., a positive test for tannin is obtained, but if reconcd. to a sirupy thickness and again dild., no tannin test is found. This test probably depends on the degree of dispersion of the tannin particles. The amt. of sol. matter after detannization was detd., including also that in 0, 15, and 20 washings for varying amts. of hide powder, and the amt. of tannin fixed obtained by deducting these from the total sol. matter. Curves of similar shape were obtained; the amt. of tannin found was lower with increased washing. Tannin fixation by hide powder depends on the degree of dispersion of or association of tannin in soln. The method is condemned. F. L. SEYMOUR-JONES

A new apparatus for the filtration of tan liquors in analysis. LÉON MATROD. *Cuir* 12, 39-40(1923).—A 500-cc. Jouan flask (Leunc Co., Paris), with a round hole in the base, and a neck 18 cm. by 3 cm., is fitted with a rubber stopper. Through the stopper passes a glass tube attached to a Berkefeld filter candle, 10 by 2.5 cm. The flask is turned upside down and connected to a suction filter flask. By this app., evapn. of

the liquor is reduced to a min. and liquor can readily be introduced by a funnel passing through the hole in the base of the flask.

F. L. SEYMOUR-JONES

**A new method of reporting extract analyses.** W. HOWALT. *J. Am. Leather Chem. Assoc.* **18**, 106-10(1923).—A suggestion to include in analysis reports the no. of lbs. of ext., non-tannin, and insol. matter per 100 lbs. tannin so that practical tanners may the more readily compare different exts.

J. A. WILSON

**The absorption spectra of tanning extracts in the ultra-violet.** DE LA BRUÈRE. *Cuir* **12**, 52-8(1923).—A chestnut and a cold sol. quebracho ext. were examd. alone and in various mixts. in the quartz spectrograph and a spectrophotometer. The curves for the coeff. of extinction ( $\log(I/I_1)$ , where  $I$  is the intensity of the incident and  $I_1$  that of the emergent ray) against wave length were plotted. The approx. detn. of the proportions of the two exts. is possible from the curves. Eight plates and a general graph are given.

F. L. SEYMOUR-JONES

**Differentiation of tannins and tanning extracts.** T. KÖRNER AND J. A. BOSSHARD. *Ledertech. Rundschau* **14**, 57-60, 65-6, 75-7(1922).—Quebracho tannin shows a higher C content than any other tanning material except cutch and gambier. Quebracho can be detected by dissolving a quantity of tanning ext. in 10 parts of water, treating the soln. with  $1/10$  of its wt. of NaCl, filtering, extg. the filtrate with EtOAc, fractionally pptg. the EtOAc soln. with alc., drying and analyzing the last fraction. Pure quebracho ext. in this way gives a C content of 60%, while with adulterated exts. lower values are obtained. Tannins can be sepd. and detected by fractional pptn. of the acetone soln. of the acetylated tannin with alc. The acetylated tannins and the products obtained by their sapon. lend themselves to differentiation. The acetylated tannins may be hydrolyzed with 5 cc. of HCl (sp. gr. 1.19), cooled, treated with 24 cc. of Wijs I soln., allowed to stand for 1 hr., dild. to 1 l., and titrated with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  soln. The I absorbed by different tannins varies, but there is little variation for one and the same tannin.

J. S. C. I.

**Chrome tanning. XII. The significance of the precipitation figure of a chrome liquor.** D. BURTON, R. P. WOOD AND A. GLOVER. *J. Soc. Leather Trades' Chem.* **7**, 37-46(1923); cf. *C. A.* **17**, 351.—The pptn. figures with NaOH for green and violet solns. of Cr alum of varied concns. and ages were detd. The pptn. figures for violet solns. increase slowly on ageing, while the green solns. slowly revert to the violet form. The pptn. figure is approx. proportional to the amt. of NaOH required for complete pptn. of the Cr. It is also a function of the hydron concn. of the soln., and the latter may be approx. calcd. from the pptn. figure. **XIII. The tanning properties of the common chrome liquors.** *Ibid.* 46-9.—Strips of limed, delimed, and bated calf skin were tanned in a series of chrome liquors,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$  reduced with sawdust and glucose,  $\text{K}_2\text{Cr}_2\text{O}_7$  reduced with  $\text{SO}_2$ , and chrome alum. These were adjusted to 0.4% Cr content and a basicity of 96 (equiv. to  $\text{CrOHSO}_4$ ). The speed of tanning was in the descending order Cr alum, sawdust,  $\text{SO}_2$ , glucose, while the pptn. figures were in the reverse order. The piece in Cr alum was the most heavily tanned and had the best feel and appearance. Speed of tanning and fixation of Cr increase with a decrease in the pptn. figures.

F. L. SEYMOUR-JONES

**The analysis of two-bath chrome liquors. The titration of dichromates with alkali.** W. R. ATKIN AND F. C. THOMPSON. *J. Soc. Leather Trades' Chem.* **7**, 50-2(1923).—The detn. of the relative amts. of chromate and dichromate in a 2-bath Cr liquor is accomplished by titrating with NaOH, with phenolphthalein as indicator. It is assumed that all dichromate is changed to chromate at the indicator color change. The end point is not sharp and examn. of the reaction on the basis of mass action and ionization shows that the change is only complete at a  $pH$  greater than 9.5, higher than that of the phenolphthalein color change. Thymolphthalein is a suitable indicator for the

reaction, the change from yellow to blue being modified by the chromate color into a change from yellow to a dirty gray; the change is sharp. It is necessary to blow CO<sub>2</sub>-free air through the soln. during titration because of the sensitivity of the indicator to atm. CO<sub>2</sub>.

F. L. SEYMOUR-JONES

**Some oak barks from Tonkin.** F. HEIM AND CERCHLEY. *Cuir* 12, 86-7(1923).—Twelve samples of bark were examd. The results are given in % total sol., tannin, non-tans, and insol., nature of tannin, character and color of leather produced. Except where otherwise stated all samples were reported as *Quercus pseudocornea*. Gié Quang, 22.5, 18.2, 4.1, 77.5, catechol, well struck through, not plump, supple and light color; soi (*Castanopsis vinnensis*), 18.4, 14.1, 4.3, 81.6, pyrogallol, not plump, little color, a little dry; gié gai (*C. sineusis*), 17.2, 13.3, 3.9, 82.8, pyrogallol, well struck through, not plump, supple, light color; soi phang, 17.3, 12.7, 4.6, 82.7, pyrogallol and catechol, not plump, supple, soft feel, little color; gié bop, 19.3, 12.2, 7.1, 80.1, pyrogallol, well struck through, not plump, soft, supple, little color; gié tuanga, 23.5, 11.9, 11.6, 76.5, pyrogallol and catechol, dry, not supple, yellowish chestnut-brown; gié xanh, 14.8, 11.4, 3.4, 85.2, catechol, dry, fairly deeply colored; soi da, 16.6, 10.2, 6.4, 83.4, pyrogallol, dry, not supple, little color; gié soi, 13.4, 9.6, 3.8, 86.6, pyrogallol, soft and supple, light chestnut brown; gié do, 12.4, 8.6, 3.8, 87.6, catechol, fairly supple and soft, pale brown color; gié den, 4.8 tannin, 3.6 non-tans, catechol; gié can, 4.6 tannin, 2.6 non-tans, catechol.

F. L. SEYMOUR-JONES

**Mangrove tanning barks from Madagascar.** F. HEIM AND E. SCHELL. *Cuir* 12, 88-94(1923).—Seven specimens were analyzed; the results are given in % water, total sol., tannins, non-tans, and insol.: honkolahy (*Rhizophora mucronata*), 14.69, 46.0, 34.96, 11.04, 39.31; tsitolona, 16.21, 34.14, 27.23, 6.91, 46.65; loby (*Carapa obovata*), 13.74, 31.06, 23.78, 7.28, 57.20; honkovavy (*Ceriops boiviniana*), 12.14, 30.9, 23.42, 7.48, 56.96; monoroma (*Heritiera littoralis*), 12.56, 18.00, 11.6, 6.4, 69.44; lovinso 11.52, 14.66, 7.94, 6.72, 73.82; afiafy (*Avicennia officinalis*), 11.78, 8.46, 0.94, 5.52, 81.76. Only honkolahy, honkovavy, and tsitolona are considered of practical importance in tanning.

F. L. SEYMOUR-JONES

**Control of the gelling point of glue.** R. E. WILSON AND W. B. ROSS. *Ind. Eng. Chem.* 15, 367-70(1923).—The addition of small amts. of chrome alum to glue solns. raises the setting point and viscosity, as per extensive data given. Practical use was made of this to prevent the draining away of glue solns. in barrel sizing. The chrome solns. slowly decrease in gelling point if kept hot, and precautions are necessary to avoid irreversible setting consequent on high local concn. of chrome alum.

J. A.

Apparatus for agitating leather coatings or other liquids (U. S. pat. 1,447,849) 1.

THIELE, LUDWIG: **The Fabrikation von Leim und Gelatine.** 2nd Ed. revised and enlarged. Leipzig: Verlagsbuchhandlung Dr. Max Jänecke. 189 pp. 80 cents. Reviewed in *Ind. Eng. Chem.* 15, 434(1923).

### 30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

**Some mechanical problems in the rubber industry.** H. C. YOUNG. *Engineering* 115, 247-51, 281-4, 312-6(1923). E. H.

**Use of magnesia in the rubber industry.** J. JUNGSMANN. *Rubber Age* 12, 408 (1923).—Apart from its use as an accelerator, MgO is recommended as an accessory ingredient in rubber compds. even when org. accelerators are used. Its effect is compared to the case-hardening of metals, in that it hardens the rubber without decreasing

its resiliency and increases its resistance to abrasion. The min. amt. should equal the amt. of S, but if the resin content of the rubber is high or if the goods are to be subjected to much pressure, abrasion or stress, the amt. should be greater. C. C. DAVIS

**The sticking of rubber.** TH. MARX AND A. ZIMMERMANN. *Caoutchouc & gutta-percha* 19, 11418-9(1922).—Dry crepe was exposed in an atm. of O to sunlight to det. the relative rate of deterioration when coagulated by various reagents. The hrs. required for complete tackiness were:  $\text{CaCl}_2$  + mwengere extract (A) 25.5,  $\text{CaCl}_2$  76.2, HOAc 76.2, madanze extract (B) 89.2, HOAc + A 89.2, A + B 94.2, B 98.5, HOAc + PhOH 98.5, A 98.5, A + B + HOAc 98.5, lime 98.5. When tackiness occurred, a sticky, semi-liquid condition first appeared, followed by a harder condition similar to varnish. Direct exposure to sunlight for varying times of wet rubber coagulated by  $\text{CaCl}_2$  resulted in no subsequent tackiness. The rubber turned dark, however, and the surface hardened somewhat. The latter is attributed to the sepn. of serum during drying. Tackiness could not be produced by exposure to light of rubber into which  $\text{H}_2\text{O}$  had been milled, nor by initial exposure when dry with subsequent addn. of  $\text{H}_2\text{O}$ . It is inferred that normal rubber is not rendered tacky by exposure to the sun even during the process of tapping, though such exposure is to be avoided on account of discoloration. C. C. DAVIS

**Current problems in laboratory practice.** ANON. *Caoutchouc & gutta-percha* 20, 11705-6(1923).—A discussion of the present limitations in identifying ingredients of rubber compds., particularly reclaimed rubber and bituminous and asphaltic substances. C. C. DAVIS

**Confirmatory tests with sodium fluosilicate.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 5, 144-5(1923); cf. *C. A.* 17, 226, 481.—In tests on a further series of samples of smoked sheet prepd. from latex contg. various amts. of  $\text{Na}_2\text{SiF}_6$  it is found that the latter retards vulcanization somewhat in a rubber-S mixt. but is without effect in a 90:10:50 rubber-S-PbO mixt. A moldy sample of smoked sheet cured more slowly both in a rubber-S and in a rubber-S-PbO mixt. than a sound sheet. G. S. WHITBY

The elasticity of latex paper (LUTTRINGER) 23.

MORGAN, SIDNEY: **The Preparation of Plantation Rubber.** London: Constable & Co., Ltd. 331 pp. 21s. net.

**Preservative for rubber latex.** S. C. DAVIDSON. U. S. 1,447,930, Mar. 6. A powd. mixt. of crystd. PhOH and NaOH.

**Ornamenting rubber.** L. MINTON. *Brit.* 188,413, Aug. 18, 1921. Powd. mica is applied to the surface of rubber articles (as distinct from rubber-coated fabrics) prior to or immediately after vulcanization. For molded articles, the surface of the mold is coated with an adhesive such as rubber soln. or petroleum jelly and powd. mica is dusted on. For pressed sheets, the plates are dusted with mica, the sheets are partially vulcanized, the plates are again dusted and the vulcanization is completed. Built up or enameled goods may be dusted either prior to or immediately after vulcanizing. Cf. 155,469 (*C. A.* 15, 1832).

